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Advanced Nanoscale Thin Film & Bulk Materials Towards Thermoelectric Power Conversion Efficiencies of 30%	
	5b. GRANT NUMBER W911NF-08-C-0058
	5c. PROGRAM ELEMENT NUMBER 7620AM
6. AUTHORS Jay Lewis, Bruce Cook	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

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14. ABSTRACT

Among a broad range of scientific and technological discoveries resulting directly from the NMP program, a number of these stand out as particularly compelling and ground-breaking. These are highlighted, below.
o   The NMP project achieved >26% efficient, 3-stage cascade with advanced materials from NMP, in addition to optimization of thermoelectric leg area-to-length ratios. Results were validated and shown to be reproducible.
o   A major breakthrough in TE solid-state heat-to-electric conversion.
o   Expected to have a significant impact on DoD portable power, energy efficiency leading to less demand on fuel

15. SUBJECT TERMS

thermoelectrics, energy harvesting, bismuth telluride, lead telluride, TAGS, thermal conductivity, nanomaterials

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Report Title

Advanced Nanoscale Thin Film & Bulk Materials Towards Thermoelectric Power Conversion Efficiencies of 30%

ABSTRACT

Among a broad range of scientific and technological discoveries resulting directly from the NMP program, a number of these stand out as particularly compelling and ground-breaking. These are highlighted, below.

o   The NMP project achieved >26% efficient, 3-stage cascade with advanced materials from NMP, in addition to optimization of thermoelectric leg area-to-length ratios. Results were validated and shown to be reproducible.

o   A major breakthrough in TE solid-state heat-to-electric conversion.

o   Expected to have a significant impact on DoD portable power, energy efficiency leading to less demand on fuel supply logistics, electric ships, quiet submarines, electric aircrafts, etc.; equally important for non-DoD applications in automotives to industrial platforms.

o   delta-doped n-type thin-film $Bi_2Te_{3-x}Se_x$ superlattices were shown to exhibit a high-ZT >2 at 300K

o   Device development leveraged low-resistivity contacts and thicker films from DARPA Active Cooling Module program

o   Improved Power Factor and ZT in n-type GaSb/InAs SL mid-temp thin-films

o   Large ZT in p-type PbTe/GeTe SL mid-temperature films

o   ZT> 1.7 was established in p-type and n-type nano-Bi_2Te_3 bulk; breakthrough TEM results and materials characterization

o   Highest ZT ever reported in p-type Bi_2Te_3 – manuscript has been accepted for publication in Nature Nanotechnology

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received   Paper

02/26/2014 14.00   J. L. Harringa, B. A. Cook, M. Besser, R. Venkatasubramanian. Improvement in the Thermoelectric Figure-of-Merit of TAGS-85 by Rare Earth Additions,
MRS Proceedings, (08 2011): 0. doi: 10.1557/opl.2011.1258

02/26/2014 1.00   Jessica Lensch-Falk, Eric S. Toberer, Yanzhong Pei, Douglas L. Medlin, G. Jeffrey Snyder. High Thermoelectric Performance in PbTe Due to Large Nanoscale Ag2Te Precipitates and La Doping,
Advanced Functional Materials, (01 2011): 241. doi: 10.1002/adfm.201000878

02/26/2014 2.00   Andrew F. May, Espen Flage-Larsen, G. Jeffrey Snyder. Electron and phonon scattering in the high-temperature thermoelectric La_{3}Te_{4?z}M_{z} (M=Sb,Bi),
Physical Review B, (03 2010): 125205. doi: 10.1103/PhysRevB.81.125205

02/26/2014 3.00   Jean-Pierre Fleurial, G. Jeffrey Snyder, Andrew F. May. Optimizing Thermoelectric Efficiency in La,
Chemistry of Materials, (05 2010): 2995. doi: 10.1021/cm1004054

02/26/2014 4.00   Fan Yang, Teruyuki Ikeda, G. Jeffrey Snyder, Chris Dames. Effective thermal conductivity of polycrystalline materials with randomly oriented superlattice grains,
Journal of Applied Physics, (08 2010): 34310. doi: 10.1063/1.3457334

02/26/2014 5.00   Eric S. Toberer, Andrew F. May, G. Jeffrey Snyder. Zintl Chemistry for Designing High Efficiency Thermoelectric Materials,
Chemistry of Materials, (02 2010): 624. doi: 10.1021/cm901956r

02/26/2014 6.00   Japheth F. Rauscher, Catherine A. Cox, Tanghong Yi, Christine M. Beavers, Peter Klavins, Eric S. Toberer, G. Jeffrey Snyder, Susan M. Kauzlarich. Synthesis, structure, magnetism, and high temperature thermoelectric properties of Ge doped Yb14MnSb11,
Dalton Transactions, (11 2010): 1055. doi: 10.1039/b920250a

02/26/2014 7.00   Ali Saramat, Eric S. Toberer, Andrew F. May, G. Jeffery Snyder. Thermal Stability and Phase Purity in Polycrystalline Ba8Ga x Ge46?x,
Journal of Electronic Materials, (01 2009): 1423. doi: 10.1007/s11664-008-0643-9

02/26/2014 8.00   D. Cederkrantz, A. Saramat, G. J. Snyder, A. E. C. Palmqvist. Thermal stability and thermoelectric properties of p-type Ba[sub 8]Ga[sub 16]Ge[sub 30] clathrates,
Journal of Applied Physics, (10 2009): 74509. doi: 10.1063/1.3236635

02/26/2014 9.00   E. M. Levin, B. A. Cook, J. L. Harringa, S. L. Bud'ko, R. Venkatasubramanian, K. Schmidt-Rohr. Analysis of Ce- and Yb-Doped TAGS-85 Materials with Enhanced Thermoelectric Figure of Merit,
Advanced Functional Materials, (02 2011): 441. doi: 10.1002/adfm.201001307

02/26/2014 10.00   Yaguo Wang, Carl Liebig, Xianfan Xu, Rama Venkatasubramanian. Acoustic phonon scattering in Bi[sub 2]Te[sub 3]/Sb[sub 2]Te[sub 3] superlattices,
Applied Physics Letters, (08 2010): 83103. doi: 10.1063/1.3483767

02/26/2014 11.00   Yanzhong Pei, Xiaoya Shi, Aaron LaLonde, Heng Wang, Lidong Chen, G. Jeffrey Snyder. Convergence of electronic bands for high performance bulk thermoelectrics,
Nature, (05 2011): 66. doi: 10.1038/nature09996

02/26/2014 12.00 Fang Fang, Robert L. Opila, Rama Venkatasubramanian, Thomas Colpitts. Preparation of clean Bi[sub 2] Te[sub 3] and Sb[sub 2]Te[sub 3] thin films to determine alignment at valence band maxima, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, (04 2011): 31403. doi: 10.1116/1.3581053

02/27/2014 15.00 Philip T. Barletta, Gary E. Bulman, Geza Dezsi, Thomas S. Colpitts, Rama Venkatasubramanian. Investigation into the thermoelectric properties of GaSb/InAs superlattice structures, MRS Proceedings, (7 2011): 0. doi: 10.1557/opl.2011.1162

TOTAL: **14**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received   Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1) F. Yang and C. Dames, "Thermal Conductivity Reduction in Bulk Nano-composites With Randomly Oriented Superlattice Grains," oral presentation at the 2010 Materials Research Society (MRS) Spring Meeting, San Francisco, CA.
2) F. Yang and C. Dames, "Thermal conductivity reduction in self-assembled lamellar materials with randomly oriented grains," oral presentation at the American Physical Society (APS) March Meeting 2010, Portland, OR.
3) Levin, L. M.; Hu, Y.-Y.; Cook, B. A.; Harringa, J. L.; Schmidt-Rohr, K.; Kanatzidis, M. G. , New insights into high-performance thermoelectric tellurides from 125Te NMR spectroscopy, American Physical Society, Inaugural Fall 2009 Meeting of the Prairie , Section of the APS, November 12-14, 2009, abstract #G2.007
4) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, Thin-film 2-di superlattices, Nano-dot Materials and Hybrid Nanostructures for Elevated Temperatures, Presentation at the 2010 Spring Materials Research Society Meeting, San Francisco, April 8, 2010.
5) R. Venkatasubramanian, Advanced Thermoelectrics for Portable Power, Energy Harvesting & Thermal Management (Invited Presentation), JHU/APL WALEX Advanced Portable Power Systems Workshop, Johns Hopkins University, Laurel, MD, June 24, 2010
6) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, High Figure of Merit Thin-film Superlattice Thermoelectric Materials and Devices (Invited Presentation), 2010 CIMTEC, 5th Forum on New Materials, Montecatini, Italy, June 18, 2010.
7) R. Venkatasubramanian, Nanoscale Approaches to Thermoelectric Energy Conversion (Invited Presentation), South Eastern Section American Physical Society Meeting, Atlanta, GA, November 12, 2009.

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received   Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received   Paper

TOTAL:

Number of Manuscripts:

Books

Received   Paper

TOTAL:

Patents Submitted

1) High Thermoelectric Performance in PbTe due to Large Nanoscale Ag2Te Precipitates and La Doping, Caltech.
2) ~~N-type Nanocrystalline Bulk Bi2Te3-xSex Material with High Thermoelectric Figure of Merit (ZT), NCSU and RTI~~ International
3) Improved Thermoelectric Alloys Based on (AgSbTe2)-(GeTe) (TAGS)," Ames Lab and RTI International.
4) U.S. Patent filed converting a provisional: "RARE EARTH-DOPED MATERIALS WITH ENHANCED THERMOELECTRIC FIGURE OF MERIT". E.M. Levin, B.A. Cook, J.L. Harringa and R. Venkatasubramanian. Publication number US20130186449 A1; Publication date Jul 25, 2013

Patents Awarded

Awards

1) R. Venkatasubramanian, R&D 100 Award, RTI International, June 2010
2) R. Venkatasubramanian, International Advisory Board, 2010 International Conference on Materials & Technologies, Italy, June 2010.
3) R. Venkatasubramanian, Focused Session Organizer – Thermoelectric Materials and Phenomena - March 2010 American Physical Society (APS) Meeting, Oregon.
4) R. Venkatasubramanian, Technical Program Committee Member – 2010 SPIE Meeting on Energy Harvesting and Storages: Materials, Devices, and Application.
5) Andrew May (Graduate Student, Caltech) received the Goldsmid Award for outstanding graduate work in thermoelectric, International Conference in Thermoelectrics, Shanghai China, May 2010.
6) Andrew May (Graduate Student, Caltech) received the Demetriades-Tsafka-Kokkalis Prize for outstanding graduate work in sustainable energy at Caltech, June 2010.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Ethan Chan	0.50	
Yaguo Wang	0.50	
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Yangzhong Pei	0.50
Ethan Chan	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Prof. Carl Koch	0.05	
Prof. Chris Dames	0.05	
Prof. Xianfan Xu	0.05	
FTE Equivalent:	**0.15**	
Total Number:	**3**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Ethan Chan
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
Rama Venkatasubramanian	0.15
Phil Barletta	0.10
Jonathan Pierce	0.20
Peter Thomas	0.35
Gordon Krueger	0.35
Thomas Colpitts	0.35
Bryson Quilliams	0.35
Brian Grant	0.25
Miguel Rivera	0.25
Rhonda Willigan	0.25
Jeffrey Snyder	0.25
Judith Stuart	0.50
Bruce Cook	0.10
Geza Deszi	0.25
Michael Mantini	0.15
FTE Equivalent:	**3.85**
Total Number:	**15**

Sub Contractors (DD882)

1 a. California Institute of Technology   **1 b.** Office of Sponsored Research

1200 E. California Blvd.

Pasadena   CA   911250001

Sub Contractor Numbers (c): 3-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): Cal Tech initiated work on mid-temp materials, after discovering that 10 to 20 nm Zn nan
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

1 a. California Institute of Technology   **1 b.** Office of Sponsored Research

Mail Code 213-6

Pasadena   CA   911250001

Sub Contractor Numbers (c): 3-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
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Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

1 a. North Carolina State University   **1 b.** Research Administration

2701 Sullivan Drive, Suite 240

Raleigh   NC   276957514

Sub Contractor Numbers (c): 1-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): Initial work at NCSU focused on processing of Bi2Te3 and Sb2Te3 ball-milled nano-pow
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 6/30/13 12:00AM

1 a. North Carolina State University   **1 b.** Research Administration & Sponsor

Box 7514

Raleigh   NC   276957514

Sub Contractor Numbers (c): 1-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): Initial work at NCSU focused on processing of Bi2Te3 and Sb2Te3 ball-milled nano-pow
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 6/30/13 12:00AM

1 a. University of California - Riverside

1 b. 200 University Office Building

Riverside   CA   925210001

Sub Contractor Numbers (c): 4-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): UC Riverside focused on the theoretical aspects of thermal conductivity of nanoscale, 2-p
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

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1 a. University of California - Riverside

1 b. 200 University Office Building

Riverside   CA   925210001

Sub Contractor Numbers (c): 4-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): UC Riverside focused on the theoretical aspects of thermal conductivity of nanoscale, 2-p
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

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1 a. University of Delaware

1 b. 210 Hullihen Hall

Newark   DE   197160099

Sub Contractor Numbers (c): 6-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): University of Delaware began their contribution to this project by measuring valence ban
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

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1 a. University of Delaware

1 b. Office of the Vice Provost for Resea
210 Hullihen Hall

Newark   DE   197163130

Sub Contractor Numbers (c): 6-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): University of Delaware began their contribution to this project by measuring valence ban
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/11 12:00AM

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1 a. United Technologies Research Center (UTRC)

1 b. 411 Silver Lane

East Hartford   CT   061181127

Sub Contractor Numbers (c): 7-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): UTRC activities were focused primarily on 2-phase Bi2Te3-based low-temperature mater
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/12 12:00AM

1 a. United Technologies Research Center (UTRC) **1 b.** 411 Silver Lane

East Hartford CT 061181127

Sub Contractor Numbers (c): 7-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): UTRC activities were focused primarily on 2-phase Bi2Te3-based low-temperature mater
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/12 12:00AM

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1 a. Ames Laboratory **1 b.**

00000

Sub Contractor Numbers (c): 5-340-0211720
Patent Clause Number (d-1): See Article XV in Contract
Patent Date (d-2):
Work Description (e): Ames Lab investigated nano-structured PbTe, to reduce lattice thermal conductivity. The
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 6/30/13 12:00AM

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1 a. Ames Laboratory **1 b.**

00000

Sub Contractor Numbers (c): 5-340-0211720
Patent Clause Number (d-1): See Article XV in Contract
Patent Date (d-2):
Work Description (e): Ames Lab investigated nano-structured PbTe, to reduce lattice thermal conductivity. The
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 6/30/13 12:00AM

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1 a. NASA, JPL **1 b.** 4800 Oak Grove Dr

Pasadena CA 91109

Sub Contractor Numbers (c): 8-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): JPL's initial focus was on optimizing low thermal conductivity rare earth compounds to a
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/12 12:00AM

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1 a. Purdue University **1 b.** Sponosored Program Services
155 S Grant Street
West Lafayette IN 479072114

Sub Contractor Numbers (c): 2-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): Purdue University contributed early on in this project to acoustic phonon transport proper
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/12 12:00AM

1 a. Purdue University

1 b. Sponsored Program Services

610 Purdue Mall

West Lafayette   IN   479072040

Sub Contractor Numbers (c): 2-340-0211720
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 6/1/97 12:00AM
Work Description (e): Purdue University contributed early on in this project to acoustic phonon transport proper
Sub Contract Award Date (f-1): 7/23/08 12:00AM
Sub Contract Est Completion Date(f-2): 7/22/12 12:00AM

Inventions (DD882)

Introduction

RTI International, California Institute of Technology, UC Riverside, Purdue University, University of Delaware, North Carolina State University, Ames Lab of Iowa State University, and United Technologies Research Center, collaborated on a 60-month effort titled "Advanced Nanoscale Thin Film & Bulk Materials Towards Thermoelectric Power Conversion Efficiencies of 30%," in response to DARPA BAA#07-21, Nano-Materials for Power (NMP). The goal of NMP was to develop thin-film superlattices and nano-bulk materials with a ZT ~ 2 between 0 and 750oC, leading to improved thermoelectric device conversion efficiencies approaching 30%. Key focus areas of this project included:

• Superlattices, nano-dots, and multi-phase nano-structured materials to reduce lattice thermal conductivity and improve electrical transport by careful control of conduction and valence band offsets, take advantage of modulation doping.
• 1st principle quantum mechanical modeling; thermodynamic modeling to predict phase stability in thin-films and nano-bulk structures.
• Synergy of theory and characterization such as TEM, NMR, femtosecond-thermo reflectance and ZT in thin-films and nano-bulk across all relevant temperature ranges.
• Advanced thin-film and bulk materials research and related device fabrication at RTI.

This summary report serves as the final project deliverable. Primary Topics included in this summary:

• Return on Investment
• Technology focus area
o Delta-doped N-type Bi2Te3-xSex:Se
o New MOCVD reactor
o Nano-dot superlattice (NDSL) in Si/Ge
o Coherent optical phonon properties in Bi2Te3/Sb2Te3 superlattices
o Mid-temperature PbTe/GeTe nanoscale thin-films
o Nano-bulk thermoelectric materials and devices
o Accomplishments of NMP "add-on" component
o Subcontractor highlights
¿ Ames Lab, JPL, U of Delaware, UC Riverside, UTRC, NCSU, Purdue
• Awards, Manuscripts, Presentations, and Intellectual Property
• Technology Insertion opportunities

NMP – Return on Investment

The NanoMaterials for Power (NMP) program resulted in a significant impact on emerging technology, generation of new fundamental knowledge, and the training of next-generation scientists. The listing below highlights some of project's noteworthy ROI.

Number of people employed, by category: 10 Graduate students, 2 post-doctoral fellows, ~15 full-time and part-time staff
Number of newly trained scientists in this area: 7 newly trained scientists in thin-film materials, bulk materials, characterization, theory, device fabrication
Number of PhD theses initiated based on this work: 5 initiated, 3 completed, 2 anticipated completions after the program end date.
Discoveries utilized on other efforts: Delta-doped Superlattices for Active Cooling Modules, DARPA, Potential $90M savings over 10-year period, anticipated by United Technologies in DoD aircraft systems employing FADEC
Intellectual Property: 8 patents and invention disclosures, across several performers
Papers published: >22 papers published including in high impact factor journals such as Nature, Adv. Functional Materials.
Presentations given: >25 presentations including 5 invited talks
Technology licenses: 3 from Caltech; 2 from RTI

Summary of key project milestones

Among a broad range of scientific and technological discoveries resulting directly from the NMP program, a number of these stand out as particularly compelling and ground-breaking. These are highlighted, below.

o The NMP project achieved >26% efficient, 3-stage cascade with advanced materials from NMP, in addition to optimization of thermoelectric leg area-to-length ratios. Results were validated and shown to be reproducible.
o A major breakthrough in TE solid-state heat-to-electric conversion.
o Expected to have a significant impact on DoD portable power, energy efficiency leading to less demand on fuel supply logistics, electric ships, quiet submarines, electric aircrafts, etc.; equally important for non-DoD applications in automotives to industrial platforms.
o ¿-doped n-type thin-film Bi2Te3-xSex superlattices were shown to exhibit a high-ZT >2 at 300K (RTI)
o Device development leveraged low-resistivity contacts and thicker films from DARPA Active Cooling Module (ACM) program
o Improved Power Factor and ZT in n-type GaSb/InAs SL mid-temp thin-films (RTI)
o Large ZT in p-type PbTe/GeTe SL mid-temperature films (RTI)
o ZT> 1.7 was established in p-type and n-type nano-Bi2Te3 bulk; breakthrough TEM results and materials characterization

(NCSU & RTI)
o   Highest ZT ever reported in p-type Bi2Te3 – manuscript has been accepted for publication in Nature Nanotechnology
o   The improved ZT was shown to directly translate to higher device efficiency (see Figure 1
o   Significant progress in low-temperature nano-Bi2Te3 bulk device performance over conventional Bi2Te3-aloy TE power generation (RTI & NCSU)
o   Nano-bulk p-type Bi2Te3-alloys with smaller nano-grains and improved ZT demonstrated for low-temp (UTRC)
o   ZT~1.8 at 700K was achieved in mid-temperature p-type Enhanced TAGS ("e-TAGS") (Ames Lab)
o   Among the highest ZT value ever reported for mid-temperature power generation materials. Manuscript published in Advanced Materials.
o   High ZT confirmed and correlated with increased device performance (see Figure 2, below).
o   Significant progress in Enhanced p-TAGS/conventional n-PbTe device over conventional p-TAGS/n-PbTe TE power generation (RTI & Ames)
o   ZT~1.8 was established at 800K in mid-temperature, multi-valley degenerate p-PbTe (Caltech)
o   First set of nano-Bi2Te3 -E-TAGS/PbTe cascade power devices showed promising results with Thot~500C and Tcold~5C (RTI)
o   Doping tuning, new compositions, including novel Zintl-phase compounds, and La3-xTe4 for high-temp (JPL)
o   JPL hi-temp couples, using baseline materials, for Thot~500C to ~1000C integrated with nano-Bi2Te3 -E-TAGS/PbTe cascade
o   Band offsets measured in PbTe-GeTe system (Delaware)
o   Framework of mean free path (MFP) distributions as a theoretical tool for understanding thermal conductivity in bulk and nanostructures and modeling of key NMP materials (UCR)

Discussion of key RTI achievements
Delta-doped N-type Bi2Te3-xSex:Se
•   "Delta-doping," is a thin film growth technique used to produce thin layers with high dopant concentration, that has allowed us to maintain high carrier mobility, while increasing the carrier concentration, and lowering the kL by increasing local anharmonicity. Growth of delta-doped N-type Bi2Te3-xSex:Se samples showed that the lattice thermal conductivity can be reduced while the power factor is enhanced. It was observed for a given period of ~60Å for delta-doping, that both power factor increases and lattice thermal conductivity decreases with increased Se delta-doping time. ZT (measured by Harman method, which includes the effect of two contacts to materials and so the "materials" ZT is estimated conservatively) was found to increase to >1.0 for a delta doping period of 30Å, significantly higher than that observed for 60Å periods.
•   Optimization of delta-doped N-type Bi2Te3-xSex:Se superlattices for improved electrical contacts demonstrated that ZT ~ 2 can be achieved. The improved electrical contacts were based on Ag at the interface layer to the thermoelectric material, and an optimized annealing cycle of the contacts. Previous work on Ag-based annealed contacts on non-delta doped N-type SL samples did not improve the ZT beyond 0.5; so, the observed ZT values in the range of 1.3 to as much as ~2 were highly encouraging. In addition, it was observed that the optimum period, where ZT was maximized in the initial study, appeared to be around ~20Å, ~30Å with an unusual minimum in ZT in between these periods. More understanding of the enhanced ZT as a function of period of delta-doping is needed in future studies beyond NMP. Again we note that the ZT measured by Harman method includes the effect of two contacts to materials, and so the "materials" ZT is estimated conservatively; this should be significantly higher than 2. In any case, the observed ZT>2 data on several N-type delta-doped Bi2Te3-xSex:Se superlattices was encouraging to meet the NMP objectives for low-temperature thin-films.
•   RTI also explored the growth of the N-type Bi2Te3-xSex materials on 6-degree-offset, mis-oriented GaAs substrates, compared to standard 2-degree-off substrates, in order to obtain smoother morphology for thicker epi films (>6 ¿m). Interestingly, we observed a ZT ~0.9 by Harman method in non-delta-doped n-type SL on such substrates, which is x1.5 better than conventional SL material on standard 2-degree-off substrates. Also, this ZT was achieved with a power factor of only 21 ¿w/cm-K2 compared to delta-doped materials which have power factors ~70 to as much as 100 ¿w/cm-K2. This illustrated that significant thermal conductivity reduction can be obtained by "smooth" growth of conventional SL films.
•   In collaboration with Purdue University, RTI investigated coherent optical phonon properties in delta-doped N-type Bi2Te3-xSex:Se superlattices. The delta-doping increases the optical phonon scattering rate, as measured by Purdue University's femtosecond photo-reflectance set-up. Coherent phonons are excited via displacive excitation or impulsive stimulated Raman scattering. Coherent phonons vibrate at sub-picosecond time scale, and can be detected using femtosecond laser pulses. Coherent phonon measurements provide information about electron-phonon scattering and phonon-phonon scattering, and can be used to understand the energy transfer process in thermoelectric materials. The acoustic phonon scattering rates are expected to be enhanced in delta-doped superlattices, compared to that seen for optical phonons here, thus lowering lattice thermal conductivities. Along with enhanced carrier mobilities, these are consistent with the observed enhanced ZT in the delta-doped superlattices in the early studies. RTI 3-¿ data on delta-doped N-type superlattices show ultra-low lattice thermal conductivities as well.
•   The study of delta doping to control the carrier levels in the delta-doped N-type Bi2Te3-xSex:Se superlattice films showed that carrier levels can be controlled precisely by adjusting the growth time, for a given delta-doping time. The in-plane power factor also showed dramatic improvement, by a factor of nearly 14 which is unprecedented by any standard, by controlling the growth time. The exceptionally high power factors were maintained at the smallest periods investigated, showing that any drop in carrier mobility is offset by enhanced Seebeck coefficient. A systematic study of ZT at 300K- measured by Harman method

that directly measures ZT as opposed to from calculating based on individual material properties that make up ZT- as a function of delta doping period and carrier concentration in the film was carried out to further understand the mechanisms of ZT enhancement. A quantum-mechanical modeling of mini-band transport due to delta doping as well as thermal conductivity measurements are in progress. These delta-doped N-type superlattices (ZT~2.4 at 300K) along with our well-understood and characterized p-type Bi2Te3/Sb2Te3 superlattices (ZT~2.4 at 300K to 2.9 at 400K) will position us well for making p-n device couples for low-temperature stage of a 3-stage power conversion cascade device.
• Final optimization of the delta-doped N-type Bi2Te3-xSex:Se superlattices resulted in a ZT ~ 2 to 2.4 at 27°C in N-type optimized Delta-doped Superlattices (DDSL) in Bi2Te3-xSex through the aforementioned enhancement in power factor and reduced lattice thermal conductivity.

New MOCVD reactor
• A new MOCVD reactor was acquired and brought online to grow III-V materials for mid and high-temp stages in support of the NMP program. Using the new MOCVD reactor RTI successfully grew III-V materials for mid and high-temp stages – in particular, InAs and GaSb on GaAs substrates. We obtained specular 2-di films of InAs on GaAs as well as InAs/GaSb multi-layer structures on GaAs substrates. It is noteworthy that we successfully produced a novel "holy" InAs structures on GaAs substrates. These "holy" InAs structures are complementary to well-observed and studied InAs nano-dots on GaAs, in the sense that the InAs film is characterized by sub-micron to hundred-nm-scale holes when grown on GaAs. Thus there is a continuous network of InAs structures, thereby avoiding quantum-confinement effects, but at the same time nanoscale to mesoscale InAs structures to lower lattice thermal conductivity, in addition to the anticipated acoustic-mismatch-related thermal conductivity reduction from InAs/GaAs interfaces. We were able to grow a GaAs smoothing layer on top of the InAs holy structures, and then repeat the growth of the InAs holy structures. The long-term vision is to create GaAs/h-InAs/GaAs/h-InAs/GaAs (where h-InAs stands for holy InAs) multilayer structures and eventually superlattices – thereby achieve a desirable high-temperature (with bandgap in between InAs and GaAs) nanoscale thin-film.
• Verification of the growth of 1nm/6nm GaSb/InAs superalttices was confirmed by Transmission Electron Microscopy. Detailed Kronig-Penny (K-P)) modeling of electron transport through these superlattices suggests an estimated e-h transition energy or effective bandgap of 0.28 eV, suggestive of use for mid-temperature applications. K-P modeling also indicated that electron transport through the thickness of the superlattices would be desirable in a mini-band formation, implying in-plane power factor would be comparable to cross-plane value. Several GaSb/InAs superlattices samples were prepared and characterized for in-plane power factor, with optimal samples characterized by power factors as high as 30.4 ¿W/cm-K2 at 300K. RTI requested UCR to carry out modeling of cross-plane thermal transport in GaSb/InAs SL to see what thermal conductivity reduction can be obtained in the material system. This modeling suggested that GaSb/InAs SL structures with thermal conductivity at 300K that could approach values as low as 2 W/m-K (for non-specular scattering) to as high as 21 W/m-K (for specular scattering) for a 10-nm period. 3-¿ measurements on the more optimal 7-nm period GaSb/InAs superlattices structures indicated a thermal conductivity of 12.2 W/m-K, about the average between specular and non-specular scattering modes. This indicates a ZT of only ~0.08 at 300K, comparable to ErAs-Nano:InGaAs/InAlAs superlattices being developed by Shakouri et al. at UCSC at 300K, but is expected to increase significantly to >1 at mid-temperature ranges (>700K). Future follow-on work to improve the power factor in GaSb/InAs SL by optimal doping is needed, as well as to develop approaches to lower the thermal conductivity closer to the 2 W/m-K range, first at 300K, and eventually for achieving ZT > 2 at elevated mid-temperatures.
Nano-dot superlattice (NDSL) in Si/Ge
• As part of the NMP project, RTI began work on understanding how to control the nano-dot formation to lay the ground work for reliable high-temperature nano-dot superlattice (NDSL) in Si/Ge and other material systems. In collaboration with Purdue University, we completed an initial investigation of coherent optical phonon properties in Bi2Te3/Sb2Te3 superlattices, which will serve as a "model" nanoscale system – due to its well-established phonon-blocking, electron-transmitting properties leading to a ZT of 2.4 at 300K (Nature 2001). It was found that the scattering rate (i.e., inverse of lifetime) of optical phonons in a superlattice is significantly higher than that of the corresponding values in Bi2Te3 and Sb2Te3; this represented the first direct measurement of coherent phonon lifetime reduction in superlattice structures, consistent with the observed reduction in thermal conductivity in superlattices. The work was published in Applied Physics Letters.
• Ge nano-dots, with diameter of ~50 to 60 nm, a height of 2 to 5 nm and a density of ~5 to 10e19/cm2, were chosen for initial thermoelectric property measurements. Ge nano-dots were uniformly capped and planarized with Si and stacked again with Ge nano-dot and another Si planarizing or smoothing layer. Such stacked Si/Ge NDSL was shown to have thermal conductivity values in the range of 2.5 W/m-K for periods of 5 nm. Several such n-type Si/Ge NDSL samples were grown and characterized for electrical power factor. Unlike 2-D Si/Ge superlattices, these NDSL structures were expected to be electrically isotropic. The highest power factor measured was about 111 ¿W/cm-K2 at 300K in a 5 nm Ge NDSL, consisting of 2nm Ge and 3 nm Si. This was measured using a differential equivalent circuit model for measured electrical transport. Using, a similar differential equivalent circuit model, pure Ge films showed power factors of 45¿W/cm-K2, which is comparable to bulk Ge. The 5 nm period n-type Si/Ge NDSL, with such a high power factor, indicated a 300K ZT as high as 1.34. This ZT would increase significantly at higher temperatures, such as 450C to 750C targeted for the high-temperatures. This ZT result is highly promising and is likely to have a significant impact in thicker NDSL materials for devices as well as p-type component materials. The p-type Si/Ge NDSL materials were found to behave comparably to the n-type materials mentioned above.
• Despite the promising results, we felt that these materials would not likely offer a near-term solution for robust for high-temperature power conversion to 800C, compared with bulk materials, to achieve the 30% NMP conversion efficiency goals. Coherent optical phonon properties in Bi2Te3/Sb2Te3 superlattices

• In collaboration with Purdue University, RTI completed an initial investigation of coherent optical phonon properties in Bi2Te3/Sb2Te3 superlattices, which serves as a "model" nanoscale system – due to its well-established phonon-blocking, electron-transmitting properties leading to a ZT of 2.4 at 300K (Nature 2001). It was observed that the phonon amplitude and mode signatures are indicative of weak electron-phonon coupling in Bi2Te3, the minority component of the Bi2Te3/Sb2Te3 superlattice, thereby increasing the scattering rate of optical phonons (inverse of lifetime) in a superlattice - significantly higher than those in Bi2Te3 and Sb2Te3. This model suggests the possibility to obtain a significant increase in scattering rates in the delta-doped N-type Bi2Te3-xSex:Se superlattices – again, due to the minority component of the delta-doped layer in the layered Bi2Te3-xSex material. Measurements indicated that the scattering rate of optical phonons increases with both delta-doping and shorter period of delta-doping.

Mid-temperature PbTe/GeTe nanoscale thin-films

• Based on published phase diagrams, GeTe exhibits a miscibility gap with PbTe, so that a solid solution is not expected near the middle of the composition range. Hence, either good 2-D layered structures or nano-dot superlattice (NDSL) structures were predicted to exhibit promising thermoelectric properties. Consequently, RTI initiated work on mid-temperature PbTe/GeTe nanoscale thin-films. The initial plan was to compare superlattice films to PbTe, GeTe and alloy films to look for enhanced mobility, lower thermal conductivity and enhanced power factor. Transmission measurements confirmed the bandgaps of PbTe and GeTe to be 0.32eV and 0.31eV, respectively, thus indicating the likelihood for very little conduction or valence band offsets in a PbTe/GeTe SL system. The 0.31 eV bandgap of GeTe was considered nearly ideal for a crystalline film, as higher bandgaps would indicate an amorphous character. This, plus the fact that the lattice constants of PbTe and GeTe are 0.645 nm and 0.600 nm respectively, gave this superlattice material system a high degree of potential success for enhanced ZT through phonon-blocking/electron transmission characteristics seen in the model "Bi2Te3/Sb2Te3" superlattice system.

• The measured power factor values resulting from the first round of film growth runs achieved values of ~20 ¿w/cm-K2 in SL films compared with ~35 ¿w/cm-K2 seen in single-layer GeTe films. The lower power factor would diminish any advantages from lattice thermal conductivity reduction with superlattices, and thus not likely to improve ZT significantly. Hence the goal for the second round of optimization was to obtain power factor in SL structures that are comparable to pure GeTe films. It was believed that the lower power factor in the GeTe/PbTe SL structure resulted from the compensation of n-type PbTe in a strongly p-type GeTe. Therefore, the goal was to minimize the PbTe component in the GeTe/PbTe SL structure. RTI requested UCR to carry out modeling of cross-plane thermal transport in GeTe/PbTe SL to see if thermal conductivity reduction could be obtained with an ultra-thin PbTe component layer. The UCR modeling predicted that GeTe/PbTe SL structures would have a thermal conductivity at 300K that approaching 0.4 W/m-K (for non-specular scattering) to 1.3 W/m-K (specular scattering). With an average thermal conductivity of 0.85 W/m-K, the estimated ZT at 300K would reach 1.4 at 300K! This ZT would increase significantly at higher temperatures, such as 150C to 450C, targeted for these mid-temperature films. The direct measurement of thermal conductivity in these superlattice films involved contact development and thermoelectric element fabrication.

• Continued study of mid-temperature PbTe/GeTe superlattice thin-films determined that a p-type PbTe/GeTe, 1 nm/10 nm superlattice, is capable of achieving a power factor as high as ~40 ¿W/cm-K2. This was a significant achievement, in spite of the potential n-type compensation of PbTe within the p-type superlattice. The superlattice quality of the 1nm/10nm PbTe/GeTe structure was confirmed by both XRD satellites and TEM imaging. The TEM showed a hybrid PbTe/GeTe 2-dimensional SL interspersed with 3-dimensional PbTe-rich nano dots. Thus, these structures are likely to exhibit a significant reduction in thermal conductivity from both a superlattice effect, creating specular scattering and any backscattering of phonons, as well as non-specular or diffused scattering. The high a power factor, plus the ability to lower thermal conductivity significantly through a superlattice approach, enables a high ZT. Temperature dependent measurements were carried out with these materials. For the P-type PbTe/GeTe SL, the fully-optimized ZT is expected to exceed 2 between 177 and 327oC due to thermal conductivity reduction and further improvement of power factor at optimal, elevated temperatures.

Nano-bulk Thermoelectric Materials and Devices

• RTI, in collaboration with NCSU, developed an approach to synthesize bulk n- and p-type chalcogenide alloy materials by high-energy mechanical ball milling and/or cryogenic ball-milling of elementary powders with subsequent densification by high-pressure uniaxial hot-pressing. We studied the influence of processing variables such as temperature, compaction time and pressure on transport properties of the resulting sintered materials. X-ray diffraction was employed in order to estimate grain size after processing. P-type Nano-Bi2Te3-xSbx bulk alloys with ultra-low thermal conductivity has achieved a ZT of 1.7 between 27°C and 100°C at RTI. Work was also carried out to apply the methods developed for p-type nano-bulk materials to corresponding n-type nano-bulk Bi2Te3-xSex materials. We demonstrated that these bulk materials exhibit a unique mixture of nanoscale features that leads to enhanced Seebeck coefficient and reduced lattice thermal conductivity, thereby achieving an average ZT of ~1.26 and ~1.7 in the 27 ºC to 100 ºC range for the n-type and p-type Bi2Te3-based materials, respectively. These new nanostructured bulk materials will serve as a potential foundation for future thermoelectric power generation applications.

• NCSU and RTI collaborated on optimization of both p- and n-type Bi2Te3-based nano-materials; this involved room temperature and/or cryogenic ball-milling followed by mechanical sintering. XRD was used to obtain grain sizes prior to compaction. In addition, RTI has obtained 6.1% conversion efficiency for the p-n nano-bulk couple made from these materials, compared to ~5.35% obtained for state-of-the-art Ferrotec conventional Bi2Te3-alloy p-n couples. (Also discussed in NCSU summary)

• Heat-to-electrical single-stage power conversion devices fabricated using the nanostructured chalcogenide alloys were shown to demonstrate a dramatic 35% device efficiency improvement compared to similar devices using state-of-the-art thermoelectric (Bi,Sb)2(Te,Se)3 materials. A typical n- p- device "couple" and a corresponding schematic diagram are shown in

Figure 3, below.

With these nanostructured chalcogenide alloy couples, peak single-stage device efficiency was between (7.2±0.25)% and (7.9±0.25)% with an average of (7.5±0.25)% at a temperature difference (¿T=Th-Tc) of 300 °C (see Figure 4, below). Commercial off-the-shelf (COTS) chalcogenide-alloy devices, on the other hand, exhibit a peak efficiency of (5.6±0.25)% at ¿T~225 °C. The devices fabricated from our nanostructured materials developed during the NMP project exhibit peak efficiency at higher temperatures (¿T~300 ºC) than the COTS devices (¿T~225 °C) because the latter employs materials produced by conventional melt-growth method, and the ZT typically peaks at lower temperature (85 and 25 °C for p and n-type), which also explains the fact that the efficiencies become comparable at smaller ¿T regime. Previous work on solar thermoelectric generators utilizing nanostructured chalcogenide alloys achieved 5.2% at ¿T = 200 °C. For the same ¿T, our devices exhibited an efficiency of (6.1±0.25)%. The >17% improvement directly reflects the higher average ZT values. High temperature performance is particularly attractive for applications in exhaust waste-heat recovery, a likely technology transition and insertion area for DoD applications.

• A major advancement, approaching the overall project goal of 30% heat-to-electrical conversion efficiency, was achieved through the development of advanced, three-stage cascade device technology. During the course of NMP, improvements in bulk materials (discussed above for the nano-bulk Bi_2Te_3-based compositions) lead to continual improvements in device efficiency. In addition, we implemented an area aspect ratio optimization process to account for unequal heat flow down the individual legs. The resulting 3-stage device was based on nano-bulk Bi_2Te_3-based materials for the lower (colder) stage, PbTe/e-TAGS for the mid-stage, and half-Heusler alloys for the hot stage, as shown in Figure 5, below.

The conversion efficiency of this material/device configuration reached a world-record 26% in multiple tests, and on multiple devices (see Figure 6, below).

• Through the NMP program, we demonstrated that an optimal hot pressing pressure is required for maximum thermoelectric power factor in different n-type Bi(Se)Te alloys, modulated mainly by the variations in the carrier concentration and thus the Seebeck coefficient. This phenomenon is attributed to the increases in the amount of positively charged antisite defects as the pressure increases to a point where their contributions are canceled out by other negatively charged antisite defects. Modifications of the energy gap resulting from the lattice distortions at high pressure also likely play a role.

• For highlights on additional bulk materials, please refer to summaries by Ames Laboratory, JPL, and UTRC in the "subcontractor" section, below.

Other Focus Areas – including NMP "add-on"

• During the project's final "add-on" period, a significant amount of progress was realized in the area of growth and characterization of the n-type GaSb/InAs superlattices, with the demonstration of 1nm/6nm GaSb/InAs superalttices by Transmission Electron Microscopy. Several GaSb/InAs superlattices samples were prepared and characterized for in-plane power factor, with optimal samples indicating power factor as high as 30.4 ¿W/cm-K^2 at 300K. For the N-type GaSb/InAs SL, a ZTave>1.4 between 177 and 377oC was estimated as a result of thermal conductivity reduction and improvement in power factor at optimal, elevated temperatures. Additional follow-on work is recommended to develop viable approaches for reducing the thermal conductivity close to 2 W/m-K, in order to achieve ZT > 2 at elevated mid-temperatures.

a. RTI achieved extraordinarily low thermal conductivity (0.03 W/m-K @ 2 nm thick) in crystalline Bi_2Te_3 thin films (partially supported by DARPA MESO program). (Ultra-thin Bi_2Te_3 films have shown potential for ZT in the range of 5 to possibly as high as ~10 at 300K.) Results were experimentally determined by two independent measurement techniques, as shown in Figure 7, below.

i. 3¿ – Measured at RTI

ii. Thermoreflectance - Measured at Purdue

• Quantum-confinement effects were also observed for the first time in one of the most important TE materials, Bi_2Te_3, through a GaAs-Bi_2Te_3-air heterostructure.

• RTI successfully developed methods for controlled synthesis of 2 nm to 58 nm films at a very precisely-regulated deposition rate of 0.04 nm/sec.

• RTI and NCSU identified Ga_2Te_3 interfacial layer via STEM measurements. This Ga_2Te_3 layer enables sharp interfaces and the epitaxial growth of Bi_2Te_3 on GaAs substrates. (Published in: APPLIED PHYSICS LETTERS 102, 081601 (2013) (see Figure 8, below).

• RTI measured as-deposited power factors of Bi_2Te_3 thin films as a function of film thickness and found the maximum power factor to be ~30 μW/cm-K^2 at a thickness of 10 nm, as shown in Figure 9, below.

• As shown in Figure 10, below, RTI subsequently achieved an improved power factor in 5 nm thick Bi_2Te_3 thin avoid evaporation of the film.

• Given the impressive power factor (130 μW/cm-K^2) and low measured cross-plane thermal conductivities, the potential for development of future, follow-on high ZT material is highly promising, as shown in Figure 11. ZT > 2.0 appears achievable assuming the modest in-plane thermal conductivity of 2 W/m-K.

• RTI also developed high power factor, high Sb-content $(BiSb)_2Te_3$ thin films

a. We note high power factor >140 μW/cm-K^2 for thin $Bi_{0.1}Sb_{1.9}Te_3$ thin films for thickness ~ 100 nm.

b. In the final year of the NMP program, we developed processes to grow similar material at a faster growth (more than 2x) rate in order to achieve thicker films (~1 μm) that could be suitable for future device fabrication. Note: The power factor of typical p-type Bi_2Te_3/Sb_2Te_3 superlattice films is ~100 μW/cm-K^2

• RTI established growth of ~30 μm thick p-type Bi_2Te_3/Sb_2Te_3 superlattice and n-type Bi_2Te_3-xSex ¿-doped alloys. To achieve the thicker films a 3-step growth process was developed wherein the growth was interrupted approximately every 10 μm to confirm the surface morphology was acceptable, and the process was then re-initiated on the same surface. Below is a

table summarizing the properties of the as-grown thin films. These thicker films will reduce parasitic losses associated with thin film device processing and improve device performance.

• RTI also collaborated with General Dynamics Land Systems (GDLS) on an ARL-funded program to evaluate TE for waste heat recovery. RTI, in collaboration with GDLS and Creare, demonstrated power levels of 80-Watts in fractional-scale, proof-of-concept tests, and RTI/GDLS have been evaluating the next phase towards a 5-kW demo and eventually to a final system of 25 to 50-kW.   The advanced TE materials on NMP (especially below 450C) and their modules are expected to fit in this roadmap.

Subcontractor Achievements
 JPL
JPL's initial focus was on optimizing low thermal conductivity rare earth compounds to achieve ZT values of 1.5 to 2.0 in the 800 to 1050 K temperature range. The current baseline materials developed for long life NASA applications, n-type La3-xTe4 and p-type Yb14MnSb11, have peak ZT values in the 1.3-1.5 range at 1275 K, close to 1.0 at 1050K and about 0.8 at 900 K. Significant (i.e., > 50%) improvements in power factor and reductions in lattice thermal conductivity were necessary to achieve the DARPA NMP goals. Tuning of the electrical properties to maximize ZT values in the targeted temperature range required a significant reduction in carrier concentration. Such reductions, from 1.2x1021 h/cm3 down to the 1019 h/cm3 range, were achieved in Al-rich Yb14Mn1-yAlySb11 (0.7=y=1.0) samples synthesized by high energy ball milling. This now enables the full impact of lattice thermal conductivity reductions onto peak ZT values, which are predicted to reach 1.5 or higher at 900 K for carrier concentrations near 1x1020 h/cm3 for the plot of ZT versus hole concentration and for 0, 25 and 50% reductions in lattice thermal conductivity. The reduction in lattice thermal conductivity were sought through three different synthetic routes: preparation and characterization of new 14-1-11 bulk compositions, nanostructuring through in-situ formation of nanoscale conductive precipitates within the 14-1-11 matrix, and nanocomposites that include nanoscale inert scattering inclusions. Synthetic techniques for all three approaches were demonstrated for the nanostructuring approaches using the baseline semi-metallic Yb14MnSb11 composition. Similar results were also achieved in the n-type La3-xTe4 system with both metallic (Ni) and insulating (SiC) nanoscale inclusions. Activities also focused on achieving precipitate and inclusion sizes below 100 nm, and ensuring a homogeneous distribution throughout the host matrix. In spite of poor control over size and distribution, the inclusions have a low impact on electrical properties in the 14-1-11 Zintls, which is key to maximizing gains in lattice thermal conductivity reductions. Hence, the prerequisites in terms of reducing hole concentration and introducing nanoscale inclusions for lower lattice thermal conductivity were accomplished through the development of suitable synthetic routes.

Ames Laboratory
Ames Lab investigated nano-structured PbTe, to reduce lattice thermal conductivity. The approach was to use the binary compound GeTe, which is known to form a spinodal region with PbTe, as a second phase in PbTe. The effort was driven by the constraint that the inclusions should be coherent with the matrix to minimize scattering of charge carriers, but possess different elastic modulus and lattice constant to introduce strain the matrix, which was expected to scatter intermediate wavelength phonons. X-ray diffraction showed evidence of two distinct phases in 40% and 50% GeTe samples.
The addition of GeTe was indeed shown to facilitate the formation of nanoscale precipitates in PbTe, as seen in the inset of Figure 12. The figure also shows the effect of GeTe additions on the Seebeck coefficient of PbTe. In order to extend these effects to obtain superior n-type PbTe, recent efforts have been focused on additions of PbI2 to PbTe+GeTe. In our initial effort, we were successful in producing a PbTe+10 mol. % GeTe nanocomposite with a 300K Seebeck coefficient of -294 µV/°C.
The encouraging observation of coherent nano-inclusions in PbTe with GeTe addition, combined with very high Seebeck coefficient values of 250 to 350 microV/K and low thermal conductivity values of ~ 8 mW/cm-K, led efforts to introduce dopants into this system in order to optimize the electrical conductivity. Samples of PbTe + 10, 20, 30, 40, and 50 mole percent GeTe were synthesized by melt processing in which 0.1% and 0.2% PbI2 were added to the initial charge. Unfortunately, work on this system was terminated before full characterization of TE properties could be measured.

In addition, Ames investigated the introduction of f-level resonant states near Fermi Energy in TAGS-85 [(AgSbTe2)15(GeTe)85] for the enhancement of Seebeck coefficient. TAGS-85 is a well-known thermoelectric material based on germanium monotelluride that exhibits a second-order displacive transformation from a high-temperature cubic to a low-temperature rhombohedral polymorph. TAGS has historically exhibited poor uniformity, with cast materials exhibiting segregation of Ge and also Ag-Te, leading to a three-phase microstructure. The presence of undesirable secondary phases is observed not only in the cast ingots, but also in hot pressed compacts as well. In general, homogeneous materials exhibit higher ZT values than inhomogeneous structures, because of the scattering effects associated with interfaces and local deviations from the optimal composition.
This program involved addition of small amounts of the rare earth elements Ce and Yb to TAGS-85, and has demonstrated a reproducible 25 to 30 percent increase in ZT at 700K in materials obtained by solidification from the melt. Analysis by x-ray diffraction of the chemically-modified alloy suggests a partial stabilization of the high-temperature cubic polymorph. 125Te NMR studies confirmed the incorporation of rare earth cations into the GeTe-based lattice. Solid state synthesis was successfully applied to the processing of rare-earth-doped TAGS-85 and has resulted in a further increase in ZT beyond the levels initially observed in melt-solidified materials.

Despite the chemical inhomogeneity, "neat" TAGS-85 exhibits a maximum ZT of ~ 1.2 to 1.3, which was increased to 1.8 for mid-temperature applications (~700K) with the addition of 1% divalent rare earths, Yb and Ce as a result of this program. As part of a broader effort to achieve higher ZT values in TAGS with rare earth additions, we have investigated process modifications to eliminate phase segregation and achieve a more uniform structure. One variable that has been recently investigated is the maximum temperature during melt processing, which had been established as 825¿C by early processing work performed in the 1970's. We have prepared TAGS-85 ingots in which the maximum temperature was increased to 900¿C and 1000¿C, in order to achieve complete dissolution of all constituents in the melt. Another processing variable that was investigated is the effect of long-term heat treatments to facilitate solid-state dissolution of the second phase inclusions. We also examined TAGS-85 with addition of Gd, a rare earth element possessing a higher magnetic moment than either Ce or Yb, in order to determine the extent to which magnetic scattering is contributing to the increase in ZT. This was necessary in order to understand the underlying physics behind the observed performance enhancement.

The temperature dependencies of the Seebeck coefficient, a, electrical conductivity, s, power factor (a2s), and thermal conductivity, ¿, were measured in samples containing rare earth additions. It was seen that the electrical conductivity remains essentially unchanged in the samples containing 1%Ce or 1%Yb, while the Seebeck coefficient is increased by ~13% at 300 K and by ~16% at 700 K. While the neat TAGS-85 at 700 K reaches a maximum power factor of 27 ¿W¿cm-1¿K-2, the rare earth-containing samples achieve a maximum power factor of 36 ¿W¿cm-1¿K-2. The effect of doping TAGS-85 with Ce or Yb on power factor is similar.

Although the thermal conductivity of TAGS-85 doped with Ce and Yb at 700 K is higher by 3-5% than that of neat TAGS-85, increase in Seebeck coefficient by 16% overcomes a negative effect from the thermal conductivity and ZT reaches 1.8 (note that ZT ¿ S2). This is one of the highest ZT values reported for bulk, p-type TE materials. Two developments were particularly encouraging. The addition of Gd produces a casting that appears to possess lower porosity than previous castings. In addition, improvements in the gas handling system used to seal quartz ampoules has led to castings of baseline TAGS that likewise appear to be of lower porosity. A complementary solid-state reaction synthesis (SSRS) technique to casting was also developed for rapid, low-cost synthesis of TAGS. This method involves powder processing techniques, including solid state reaction synthesis, to produce fine grained, highly-homogeneous bulk materials.

Cal-Tech
Cal Tech initiated work on mid-temp materials, after discovering that 10 to 20 nm Zn nanoparticles remain dispersed in Zn4Sb3, a mid-temperature/high-temperature material. They also looked at PbTe nano composites, drawing inspiration from their work on earlier efforts involving PbTe-Sb2Te3 nano-composites. Cal Tech was asked to complete identification and plans for candidate materials for hi-temperature stages. Cal Tech was encouraged to bring in the expertise of JPL in producing La3Te4 nano-composites (hi-temp N-type) and Yb14MnSb11 (hi-temp P-type) materials. Specifically, they have provided a high-temp p-type Yb14MnSb11 roadmap and an n-type La3Te4 roadmap. They initiated work on high-temp materials and have reported one of the first nanocomposite in La3Te4 with a refractory second phase precipitate; they also examined PbTe and other dopants as the second-phase precipitate. They projected a ZT >1 to as much as 1.2 in this N-type La3Te4 high-temperature material. Their goal was to reduce lattice thermal conductivity in Yb14MnSb11 by composite formation. In the mid-temperature materials development, Cal Tech developed a PbTe-Ag2Te nanocomposite, in which nano-particle/second phase are formed at ~500oC. Particles with size of 5 nm have been observed in TEM. A potential ZT in the range of 1.5 was achieved at ~ 500oC in these n-type materials, to complement advanced p-TAGS developed by Ames Lab and described above.
As part of this combined effort, JPL was able to complete the synthesis of 6 new 14-1-11 Zintl compositions derived from the baseline p-type Yb14MnSb11. Five of the six new compositions showed some amount of the desired 14-1-11 stoichiometry; these include Yb14GaSb11, Yb14InSb11, Yb14CdSb11, Eu14MnSb11 and Yb13NbSb11. P-type Yb14MnSb11 composites with ZT~1.4 at ~900°C using BN nano-inclusions were obtained. Even though we measure all of the thermoelectric properties, electron microscopy has shown that we have second phases present. New Zintl compositions were also attempted; Zintl phases had not been reported before and some tuning of the processing parameters were necessary before achieving synthesis of single phase samples. For further advancing n-type La3-xTe4, JPL synthesized nano-composites using inert inclusions such as Si3N4. YbTe inclusions into Yb14MnSb11 were also attempted. Separating the various phonon scattering mechanisms and the electronic contribution to the thermal conductivity presented a significant challenge to understanding, and further optimizing, these nanocomposites. Caltech has shown that relatively large nanometer-scale (50-200nm) Ag2Te precipitates in PbTe can be controlled according to the equilibrium phase diagram and that these materials show intrinsic semiconductor behavior with high electrical resistivity, enabling direct measurement of the phonon thermal conductivity. Their study provided direct evidence that even relatively large, nanometer-scale microstructures reduce thermal conductivity below that of a macro-scale composite of saturated alloys with Kapitza-type interfacial thermal resistance at the same overall composition. Carrier concentration control was achieved via La doping, enabling independent control of the electronic properties and microstructure. These materials exhibited lattice thermal conductivity that approaches the theoretical minimum above ~650K, even lower than that found with small nanoparticles. Optimally La-doped n-type PbTe-Ag2Te nanocomposites exhibit zT > 1.5 at 775 K.

North Carolina State University
Initial work at NCSU focused on processing of Bi2Te3 and Sb2Te3 ball-milled nano-powders using liquid-nitrogen ball-milling for nano-powders starting high purity individual component elements; they were able to produce nanocrystalline powders of 10nm average grain size with desired composition in both p-type and n-type systems. According to XRD analyses, the peak

position and relative intensity were well matched with the target composition, i.e. Bi2Te2.7Se0.3 (N-type) and Bi0.4Sb1.6Te3 (P-type) respectively. The nano-powder consolidation indicated that good materials can be obtained from both room temperature and high temperature compaction process; while the former gives zero grain growth, the later method maintains grain size less than 30nm.

NCSU studied the influence of factors such as temperature, compaction time and pressure on properties of resulting sintered materials. NCSU optimized the processing parameters and again XRD was used to obtain grain size after processing. Bi2Te3 and Sb2Te3 ball-milled nano-powders were used for p-type materials. NCSU prepared nano-crystalline Bi2Te2.7Se0.3 as well, by ball milling the elemental powders at either 77K or room temperature. The as-milled powders had fine nano-crystalline grain sizes which were estimated from x-ray diffraction line broadening. Samples milled at 77K had an average grain size of 8 nm. Those milled at room temperature had an average grain size of about 13 nm. The powders were consolidated by hot pressing in tungsten carbide dies under pressure of 2 GPa in an argon atmosphere at temperatures ranging from 200oC to 410oC, the latter near the melting point of the material.

As expected, the density of compacts increased with increasing compaction temperature and the electrical resistivity, presumably reflecting the decrease in porosity, also decreased with increasing compaction temperature. RTI measured all the thermoelectric properties of NCSU's nano-bulk materials including electrical resistivity by Hall-effect, Seebeck coefficient and bulk thermal conductivity by a finely calibrated q-meter. The best thermoelectric properties were observed on samples compacted around 400oC. The best 300K ZT in p-type materials were 1.07 at 300K, 0.96 at 323K and 1.0 at 373K. The ZT values were not as high as in the UTRC nano-bulk p-type materials, described below. The p-type materials had good power factors, slightly higher than conventional bulk materials, but the thermal conductivities were not any lower than in bulk materials; thus the ZT improvement over conventional bulk p-type materials was marginal at best. On the other hand, the N-type nano-crystalline materials showed a very large ZT, as high as 1.76 at 300K, 1.66 at 323K and 1.5 at 373K. The increase in ZT is largely due to the excellent preservation of power factor in the nano-bulk materials while at the same time having a nearly factor of two smaller thermal conductivity than conventional bulk N-type materials. This represented the first observation of enhanced ZT at 300K in N-type Bi2Te3-based nano-bulk material by any group in the world, to our knowledge.

Thinning of the samples TEM was carried out by focused ion beam machining of these n-type samples. The samples typically had an average grain size of about 400 nm. The best p-type sample had an average grain size of about 1000 nm. No extra phases were noted in the n-type material by either x-ray diffraction or TEM, unlike the p-type material which had Te precipitates. In addition, RTI obtained ~8% conversion efficiency for the p-n nano-bulk couple made from these materials, compared to ~5.35% obtained for state-of-the-art Ferrotec conventional Bi2Te3-alloy p-n couples.

Purdue

Purdue University contributed early on in this project to acoustic phonon transport property measurements, starting with p-type Bi2Te3/Sb2Te3 superlattices. Also, they upgraded their system to allow thermal property measurements of various materials at elevated temperatures. Purdue established a photoacoustic thermal property measurement apparatus and the corresponding numerical model for characterizing thermal properties, and used it for a number of materials including thermoelectric materials. The working temperature of this system ranges from cryogenic up to about 100oC. In addition, a laser thermal reflectance measurement system (funded by another project), was expanded from room temperature to 700oC, which was used for this NMP project. Purdue developed acoustic phonon scattering measurement methods for nano-engineered thermoelectric materials, and also samples of bulk films for comparison. Acoustic phonons are excited using a femtosecond pulse at the front of the sample surface, then measured when they are reflected back to the surface from the thin film – substrate interface using another femtosecond laser beam. The goal of these measurements was to understand the nature of phonon scattering in nano-structured thermoelectric materials, and therefore to understand the thermal conductivity reduction in these materials.

Results indicated that there is significant phonon scattering in superlattices, whereas the scattering in bulk film samples is insignificant. Further analyses indicated a decrease of acoustic phonon velocity, possibly resulted from folding and flattening of phonons branches. Therefore, both the interface scattering and a reduced phonon group velocity contribute to suppressing the heat transfer process. In addition, the deviations from acoustic mismatch theory have been observed. A paper was published in Appl. Phys. Lett.

UC Riverside

UC Riverside focused on the theoretical aspects of thermal conductivity of nanoscale, 2-phase material systems as well as thermal rectification approaches to enhance ZT. As part of this effort, a phonon transport model was developed for PbTe-Sb2Te3 nano-bulk material using an independent-layer analysis approach. The model predicted that the cross-plane thermal conductivity should be reduced even at larger periods; however, in-plane specularity is a key; about 70% of net thermal conductivity in a nano-bulk comes from in-plane direction while only about 30% from the cross-plane effects. Modeling of thermal rectification approaches to enhance ZT were conducted; optimization trends suggested that 2 staggered layers are better than 1, and an extended analysis to include diffuse inclusions (a year 2 milestone) shows rectification is reduced, but still present, even for zero specularity. Recall that the specularity, p, is defined such that smooth surfaces with p=1 are perfectly specular (e.g. transmission obeys an analogue of Snell's Law) while rough surfaces with p=0 are perfectly diffuse (e.g. transmitted phonons are scattered in many directions). UCR used a semi-classical phonon model that treats the phonons as

incoherent particles (i.e., neglects wave interference effects), and the fundamental strategy was to obtain numerical solutions of the Boltzmann transport equation (BTE). A key advance is that the model accounts for the frequency dependence of the bulk phonon scattering mechanisms both in-plane and cross-plane, which had been neglected in previous BTE solutions for the cross-plane thermal conductivity.

In the area of thermal rectification, UCR validated the low-bias limit of Landauer / Bose-Einstein simulations for transport across a thin film and correctly captured the distinction between "emitted temperature" and "local equilibrium temperature" - important for these highly non-equilibrium problem. In addition, UCR provided modeling of the thermal transport in two other material systems that were investigated – PbTe/GeTe (in both thin-film superlattice form at RTI and in nano-bulk form at Ames Lab) and InAs/GaSb (in thin-film superlattices) both for mid-temperature applications.

UCR also carried out preliminary modeling of mean free path distributions in bulk and nanostructures. The various well-established models for frequency-dependent bulk phonon scattering (such as Holland, Klemens, and Callaway) can usually be adjusted to give excellent agreement with experiments for bulk thermal conductivity, but when these same models are applied to nanostructures the predictions no longer agree with each other. UCR concluded the program by developing a modeling framework to interpret this distinction in terms of the distributions of various mean free paths (MFPs) that contribute to thermal conductivity in bulk and nanostructures. An important initial observation was that the various established models place very different emphasis on long vs. short MFPs in bulk.

University of Delaware

University of Delaware began their contribution to this project by measuring valence band and conduction band offsets in material pairs that could be used to create novel, nanoscale thermoelectric composites. The first set of material systems considered was Bi_2Te_3 and Sb_2Te_3, the two components of the "model" p-type Bi_2Te_3/Sb_2Te_3 SL. Univ. of Delaware utilized the Stanford Linear Accelerator Center (SLAC) beam line to measure valence band energies; a significant effort was made in removing the native oxides, through appropriate chemical cleaning procedures, from the Bi_2Te_3 and Sb_2Te_3 materials; this was a joint collaborative work between Delaware and RTI. Initial results from SLAC measurements indicated that the two valence bands are close to each other and also the valence band maximums are close to the Fermi level energy, within the limits of noise in the measurements. Results on delta-doped N-type $Bi_2Te_3-xSe_x$:Se superlattices – the respective surfaces of a bare N-type $Bi_2Te_3-xSe_x$ layer and a Se-dosed layer – indicate that the valence-band energies (and hence conduction band energies, as the bandgap is not expected to be altered by Se dosing) are aligned within experimental error; this is favorable for cross-plane electron transport in the delta-doped N-type $Bi_2Te_3-xSe_x$:Se superlattices, potentially supporting the observation of enhanced ZT. A detailed publication of the valence-band energies in the p-type Bi_2Te_3/Sb_2Te_3 SL system was prepared.

UTRC

UTRC activities were focused primarily on 2-phase Bi_2Te_3-based low-temperature material systems, fabricating nanostructured bismuth telluride, antimony telluride, and bismuth telluride selenide structures initially containing nano-scale inclusions of silver telluride. Additional inclusion phases were also explored. In UTRC's initial studies with the p-Bi-Ag-Te system, Ag_2Te phase segregated to grain boundaries, and there was a need to develop process to improve 2nd phase distribution. Also, the Ag_2Te phase was larger than desired; so there was also a need for process modification in order to reduce 2nd phase size. In one particular composition (Sample#NMP-18), $(Sb_1.5Bi_0.5Te_3)0.975(Ag_2Te)0.025$, UTRC observed that the power factor (defined as $¿2T¿$) was 0.74 W/m-K compared to 0.59 in conventional p-$Sb_1.5Bi_0.5Te_3$ alloy (Sample#NMP-17). UTRC also carried out detailed SEM electron back-scattered imaging, mapping for the Bi, Te, Sb and Ag composition profiles in the NMP-18 sample; it was observed that the matrix phase was Sb-deficient and the precipitate or second phase was Sb/Bi rich. Additional work involved consolidating pellets from mechanically milled powders. All material fabrication was targeted at producing a high ZT, p-type TE nanocomposite sample in the Sb/Ag/Bi/Te material system. The best ZT value measured was 0.48. Interestingly, this value of ZT can be obtained through either a direct solidification route or through a powder processing + hot pressing route. Based on a round of thermoelectric data, it appeared that the composite samples prepared were all in an over-doped state. The electrical resistivity value was too low (< 1 mohm-cm), while the Seebeck coefficent values were also too low, much less than the desired 180-200 ¿V/K. To raise the resistivity and Seebeck coefficient of these materials, another round of material fabrication was conducted in which both (i) the Ag/Sb ratio within the $AgSbTe_2$ phase, and (ii) the post-solidification heat treatment step was altered. An objective of this study was to determine if this material could yield a ZT~1.2 value at 300K, as reported earlier. The second objective was to determine if a material derived from chemical elements would give its peak ZT at a different temperature than the one derived from a commercial ingot. It was expected that the doping levels between these two materials would vary. In such a case, one might be able to "tune" the peak ZT across a wide temperature range by varying the doping levels. However, this did not yield a high ZT result; the best ZT achieved was only 0.94, not 1.2; the electrical resistivity values were higher in comparison, suggesting the need to incorporate additional dopants. However, in subsequent studies at UTRC, a ZT value of 1.35 was obtained. This higher ZT value was achieved by taking the ZT~1.2, p-type nanostructured material (from commercially procured $Sb_1.5Bi_0.5Te_3$ material) and applying a low temperature anneal to remove residual defects in the structure. Upon careful review of the thermal conductivity data and the sample measured, it was recognized that the cut sample had a surface with varying thickness. Depending upon the thickness input into the calculation for thermal diffusivity, different values were obtained which resulted in an uncertain ZT. At best the ZT value was 1.35, however

in all likelihood, the sample's true ZT is somewhere between ZT ~1.2 and 1.35.

In order to reduce the uncertainty, new samples were fabricated and tested in the p-type nano-bulk area. A new batch of commercial grade, bulk (not nano-structured), p-type ingot material (Sb1.5Bi0.5Te3) was sourced. This material was used as the starting material to fabricate a high ZT, nanostructured p-type material. The objective was to compare the ZT properties from multiple process methods and then determine which route produces the best microstructure and properties. Best P-type Nano-BixSb2-xTe3 bulk alloy made by UTRC exhibited a ZT of 1.3 near 27°C.   Subsequent activities at UTRC were focused on delivering a material with a ZT~1.5. Spark plasma sintering was explored as an alternative consolidation technique to graphite hot pressing. The use of shorter milling times, cryo-milling, and low voltage SPS was also explored as various methods to reduce the final grain size.

Awards/Manuscripts/Presentations/IP
Papers published in peer-reviewed journals

1)   Yanzhong Pei, Jessica Lensch-Falk, Eric S. Toberer, Douglas L. Medlin, and G. Jeffrey Snyder "High Thermoelectric Performance in PbTe due to Large Nanoscale Ag2Te Precipitates and La Doping" Advanced Functional Materials (in press)
2)   A.F. May, Espen Flage-Larsen, and G. J. Snyder " Electron and phonon scattering in the high-temperature thermoelectric La3Te4-zMz (M=Sb,Bi)" Physical Review B 81, 125205 (2010)
3)   F. May, J. –P. Fleurial and G. J. Snyder "Optimizing Thermoelectric Efficiency in La3-xTe4 via Yb Substitution" Chemistry of Materials, 22, 2995 (2010)
4)   F. Yang, T. Ikeda, G. J. Snyder, and C. Dames "Effective thermal conductivity of polycrystalline materials with randomly oriented superlattice grains" J. Appl. Phys. 108, 034310 (2010)
5)   E. S. Toberer, A. F. May and G. J. Snyder "Zintl Chemistry for Designing High Efficiency Thermoelectric Materials" Chemistry of Materials, 22, 624 (2010)
6)   J. F. Rauscher, C. A. Cox, T. Yi, P. Klavins, E. S. Toberer, G. J. Snyder, S. M. Kauzlarich, "Synthesis, Structure, Magnetism, and High Temperature Thermoelectric Properties of Ge doped Yb14MnSb11" Dalton Trans. 39, 1055 (2010).
7)   F. May, Eric S. Toberer, Ali Saramat, G. J. Snyder "Characterization and analysis of thermoelectric transport in n-type BaGaGe" Physical Review B 80, 125205 (2009).
8)   Ali Saramat, Eric S. Toberer, Andrew F. May and G. Jeffery Snyder "Thermal Stability and Phase Purity in Polycrystalline Ba8GaxGe46-x" J. Electronic Mater. 38, 1423 (2009).
9)   D. Cederkrantz, Ali Saramat, G. Jeffery Snyder and A. E. C. Palmqvist "Thermal stability and thermoelectric properties of p-type Ba8Ga16Ge30 clathrates" J. Apl. Phys. 106, 074509 (2009.
10) E. M. Levin, B. A. Cook, J. L. Harringa, S. L. Bud'ko, R. Venkatasubramanian, and K. Schmidt-Rohr, "Analysis of Ce- and Yb-doped TAGS-85 Thermoelectric Material with Enhanced Figure-of-Merit, Advanced Functional Material (in press)
11) Yaguo Wang, Carl Liebig, Xianfan Xu, and Rama Venkatasubramanian, Acoustic phonon scattering in Bi2Te3/Sb2Te3 superlattices, Appl. Phys. Lett. 97, 083103 (2010); doi:10.1063/1.3483767.

12) Convergence of electronic bands for high performance bulk thermoelectric, Yanzhong Pei1, Xiaoya Shi, Aaron LaLonde, Heng Wang, Lidong Chen & G. Jeffrey Snyder, Nature 473, p66 (2011) – by our NMP team member, Caltech.

13) Preparation of clean Bi2Te3 and Sb2Te3 thin films to determine alignment at valence band maxima, F. Fang, R. Opila, R. Venkatasubramanian, & T. S. Colpitts, Journal of Vacuum Science and Technology A 29, 031403 (2011).

14) U.S. Patent filed converting a provisional: "RARE EARTH-DOPED MATERIALS WITH ENHANCED THERMOELECTRIC FIGURE OF MERIT". E.M. Levin, B.A. Cook, J.L. Harringa and R. Venkatasubramanian.

15) Barletta, P., Bulman, G. E., Dezsi, G., Quilliams, A. B., & Venkatasubramanian, R, Investigation of the Thermoelectric Properties of GaSb/InAs Superlattice Structures. Proceedings of MRS Spring Meeting, San Francisco, CA .

16) Koch, C. C., Chan, T. E., & Venkatasubramanian, R., Thermoelectric Material Efficiency Improvements by Microstructural Refinement. Presentation at 2011 MRS Spring Meeting, San Francisco, CA (April 2011).

17) B. Cook et al., The Evolution of TAGS: Rare Earth Additions for High ZT," Presented at the 2011 MRS Spring Meeting, San Francisco, CA (April 2011).

Presentations in meetings and not published in conference proceedings

1) F. Yang and C. Dames, "Thermal Conductivity Reduction in Bulk Nano-composites With Randomly Oriented Superlattice Grains," oral presentation at the 2010 Materials Research Society (MRS) Spring Meeting, San Francisco, CA.
2) F. Yang and C. Dames, "Thermal conductivity reduction in self-assembled lamellar materials with randomly oriented grains," oral presentation at the American Physical Society (APS) March Meeting 2010, Portland, OR.
3) Levin, L. M.; Hu, Y.-Y.; Cook, B. A.; Harringa, J. L.; Schmidt-Rohr, K.; Kanatzidis, M. G. , New insights into high-performance thermoelectric tellurides from 125Te NMR spectroscopy, American Physical Society, Inaugural Fall 2009 Meeting of the Prairie , Section of the APS, November 12-14, 2009, abstract #G2.007
4) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, Thin-film 2-di superlattices, Nano-dot Materials and Hybrid Nanostructures for Elevated Temperatures, Presentation at the 2010 Spring Materials Research Society Meeting, San Francisco, April 8, 2010.
5) R. Venkatasubramanian, Advanced Thermoelectrics for Portable Power, Energy Harvesting & Thermal Management (Invited

Presentation), JHU/APL WALEX Advanced Portable Power Systems Workshop, Johns Hopkins University, Laurel, MD, June 24, 2010

6) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, High Figure of Merit Thin-film Superlattice Thermoelectric Materials and Devices (Invited Presentation), 2010 CIMTEC, 5th Forum on New Materials, Montecatini, Italy, June 18, 2010.

7) R. Venkatasubramanian, Nanoscale Approaches to Thermoelectric Energy Conversion (Invited Presentation), South Eastern Section American Physical Society Meeting, Atlanta, GA, November 12, 2009.

Manuscripts under review and/or accepted for publication

1) Fang Fang, Robert L. Opila, Rama Venkatasubramanian and Thomas Colpitts, Valence Band Maxima Offset Measurements on Bi2Te3, Sb2Te3 Thin Films for Thermoelectric Superlattice Engineering, Submitted to Appl. Phys. Lett.,.

2) Tsung-ta E. Chan, James M. LeBeau, Rama Venkatasubramanian, Peter Thomas, Judy Stuart, and Carl C. Koch, "Carrier Concentration Modulation by Hot Pressing Pressure in N-type Nanostructured Bi(Se)Te Alloy," Accepted for publication in Applied Physics Letters.

3) Tsung-ta E. Chan, Rama Venkatasubramanian, James M. LeBeau, Ryan M. White, Peter Thomas, Judy Stuart, and Carl C. Koch, "High Efficiency Thermoelectric Devices Using Nanostructured Chalcogenide Alloy Materials," Accepted for publication in Nature Nanotechnology.

Honors and Awards

1) R. Venkatasubramanian, R&D 100 Award, RTI International, June 2010
2) R. Venkatasubramanian, International Advisory Board, 2010 International Conference on Materials & Technologies, Italy, June 2010.
3) R. Venkatasubramanian, Focused Session Organizer – Thermoelectric Materials and Phenomena - March 2010 American Physical Society (APS) Meeting, Oregon.
4) R. Venkatasubramanian, Technical Program Committee Member – 2010 SPIE Meeting on Energy Harvesting and Storages: Materials, Devices, and Application.
5) Andrew May (Graduate Student, Caltech) received the Goldsmid Award for outstanding graduate work in thermoelectric, International Conference in Thermoelectrics, Shanghai China, May 2010.
6) Andrew May (Graduate Student, Caltech) received the Demetriades-Tsafka-Kokkalis Prize for outstanding graduate work in sustainable energy at Caltech, June 2010.

List of Patent Titles submitted/filed for patents

1) High Thermoelectric Performance in PbTe due to Large Nanoscale Ag2Te Precipitates and La Doping, Caltech.
2) N-type Nanocrystalline Bulk Bi2Te3-xSex Material with High Thermoelectric Figure of Merit (ZT), NCSU and RTI International
3) Improved Thermoelectric Alloys Based on (AgSbTe2)-(GeTe) (TAGS)," Ames Lab and RTI International.

Technology Transfer and Insertion

This project directly resulted in a number of technology insertion opportunities for DoD and other application spaces. A few of these are highlighted, below.

1) Delta-doped n-type superlattice structures developed under NMP are being evaluated with DARPA/ACM support and partnership with United Technologies/Hamilton Sundstrand for thermal management of electronics in DoD aircraft systems for potential benefits in combat maneuver and maintenance cost reduction.

2) Fractional-scale demonstration of Waste Heat Energy Harvesting achieved ~80-Watts from a system deployment on an M1/A1 Abrams tank at General Dynamics Land Systems (GDLS) on a TE-system-related project with US Army. The advanced NMP materials will play a role in higher efficiency values in subsequent scale-up efforts. GDLS engineers report that a 5 to 25 kW waste-heat demo using TE on top of their typical "18-kW" alternator could significantly enable new operational capability. This may fit in areas such as higher efficiency of vehicles and generators in forward operational base, to reduce fuel usage.

3) On-board power for hypersonic vehicles via solid state energy harvesting. High-temperature thermoelectric energy conversion offers a unique approach to harvest energy from available waste heat in the operation of DoD hypersonic vehicles. The technology can reduce the dependence on batteries and reduce their weight contribution, leading to extended range. Recent demonstrations of NMP-generated TE technology, performed in collaboration with Wright-Patterson AFB and Lockheed-Martin Space Systems, have shown that power densities on the order of 3.5 W/cm2 can be expected under typical thermal conditions encountered in hypersonic vehicles. Several potential locations offering adequate space and thermal profiles have been identified.

4) On-board power and thermal signature reduction in rotary aircraft platforms. Discussions were initiated with a major DoD supplier to investigate the use of NMP TE technology In rotary aircraft. The platform's engines produce on the order of 5MW of waste heat with primary exhaust nozzle temperatures on the order of 350¿C to 450¿C – thermal energy that not only could be

converted into usable electrical power, but also increases the platform's thermal signature. High-efficiency TE energy harvesting modules offer an attractive, high-reliability solution.

Technology Transfer

"Advanced Nanoscale Thin Film & Bulk Materials Towards Thermoelectric Power Conversion Efficiencies of 30%"

DARPA-DSO Contract no. W911NF-08-C-0058

FINAL REPORT

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Introduction

RTI International, California Institute of Technology, UC Riverside, Purdue University, University of Delaware, North Carolina State University, Ames Lab of Iowa State University, and United Technologies Research Center, collaborated on a 60-month effort titled "Advanced Nanoscale Thin Film & Bulk Materials Towards Thermoelectric Power Conversion Efficiencies of 30**%,"** in response to DARPA BAA#07-21, Nano-Materials for Power (NMP). The goal of NMP was to develop thin-film superlattices and nano-bulk materials with a ZT ~ 2 between 0 and 750°C, leading to improved thermoelectric device conversion efficiencies approaching 30%. Key focus areas of this project included:

- Superlattices, nano-dots, and multi-phase nano-structured materials to reduce lattice thermal conductivity and improve electrical transport by careful control of conduction and valence band offsets, take advantage of modulation doping.

- 1st principle quantum mechanical modeling; thermodynamic modeling to predict phase stability in thin-films and nano-bulk structures.

- Synergy of theory and characterization such as TEM, NMR, femtosecond-thermo reflectance and ZT in thin-films and nano-bulk across all relevant temperature ranges.

- Advanced thin-film and bulk materials research and related device fabrication at RTI.

This summary report serves as the final project deliverable. Primary Topics included in this summary:

- Return on Investment
- Technology focus area
    - Delta-doped N-type $Bi_2Te_{3-x}Se_x$:Se
    - New MOCVD reactor
    - Nano-dot superlattice (NDSL) in Si/Ge
    - Coherent optical phonon properties in Bi_2Te_3/Sb_2Te_3 superlattices
    - Mid-temperature PbTe/GeTe nanoscale thin-films
    - Nano-bulk thermoelectric materials and devices
    - Accomplishments of NMP "add-on" component
    - Subcontractor highlights
        - Ames Lab, JPL, U of Delaware, UC Riverside, UTRC, NCSU, Purdue
- Awards, Manuscripts, Presentations, and Intellectual Property
- Technology Insertion opportunities

NMP – Return on Investment

The NanoMaterials for Power (NMP) program resulted in a significant impact on emerging technology, generation of new fundamental knowledge, and the training of next-generation scientists. The listing below highlights some of project's noteworthy ROI.

Number of people employed, by category: 10 Graduate students, 2 post-doctoral fellows, ~15 full-time and part-time staff

Number of newly trained scientists in this area: 7 newly trained scientists in thin-film materials, bulk materials, characterization, theory, device fabrication

Number of PhD theses initiated based on this work: 5 initiated, 3 completed, 2 anticipated completions after the program end date.

Discoveries utilized on other efforts: Delta-doped Superlattices for Active Cooling Modules, DARPA, **Potential $90M savings over 10-year period, anticipated by United Technologies in DoD aircraft systems employing FADEC**

Intellectual Property: 8 patents and invention disclosures, across several performers

Papers published: >22 papers published including in high impact factor journals such as *Nature*, *Adv. Functional Materials*.

Presentations given: >25 presentations including 5 invited talks

Technology licenses: 3 from Caltech; 2 from RTI

Summary of key project milestones

Among a broad range of scientific and technological discoveries resulting directly from the NMP program, a number of these stand out as particularly compelling and ground-breaking. These are highlighted, below.

- o **The NMP project achieved >26% efficient, 3-stage cascade with advanced materials from NMP, in addition to optimization of thermoelectric leg area-to-length ratios. Results were validated and shown to be reproducible.**

    - o A major breakthrough in TE solid-state heat-to-electric conversion.

    - o Expected to have a significant impact on DoD portable power, energy efficiency leading to less demand on fuel supply logistics, electric ships, quiet submarines, electric aircrafts, etc.; equally important for non-DoD applications in automotives to industrial platforms.

- o **Δ-doped n-type thin-film $Bi_2Te_{3-x}Se_x$ superlattices were shown to exhibit a high-ZT >2 at 300K** (RTI)

    - o Device development leveraged low-resistivity contacts and thicker films from DARPA Active Cooling Module (ACM) program

    - o Improved Power Factor and ZT in n-type GaSb/InAs SL mid-temp thin-films (RTI)

    - o Large ZT in p-type PbTe/GeTe SL mid-temperature films (RTI)

- o **ZT> 1.7 was established in p-type and n-type nano-Bi_2Te_3 bulk;** breakthrough TEM results and materials characterization (NCSU & RTI)

    - o Highest ZT ever reported in p-type Bi_2Te_3 – a manuscript has been accepted for publication in Nature Nanotechnology

    - o The improved ZT was shown to directly translate to higher device efficiency (see Figure 1, below)
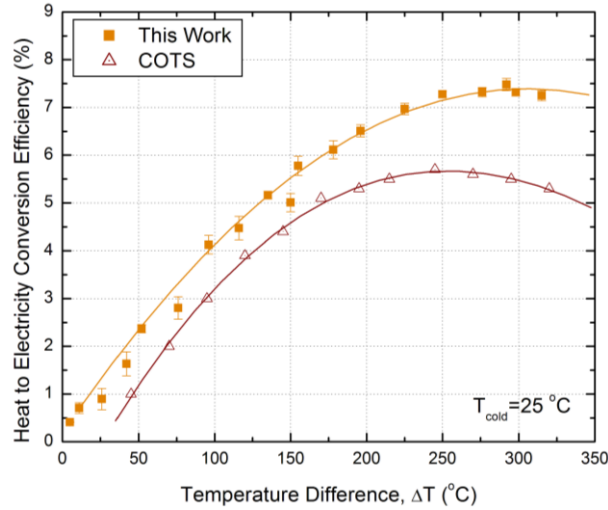
Figure 1. Comparison of RTI's improved nano-bulk Bi_2Te_3 materials in single-couple devices (upper curve) with conventional commercial materials (lower curve).

- Significant progress in low-temperature nano-Bi_2Te_3 bulk device performance over conventional Bi_2Te_3-aloy TE power generation (RTI & NCSU)

- Nano-bulk p-type Bi_2Te_3-alloys with smaller nano-grains and improved ZT demonstrated for low-temp (UTRC)

- **ZT~1.8 at 700K was achieved in mid-temperature p-type Enhanced TAGS ("e-TAGS")** (Ames Lab)

  - Among the highest ZT value ever reported for mid-temperature power generation materials. Manuscript published in Advanced Materials.

  - High ZT confirmed and correlated with increased device performance (see Figure 2, below).
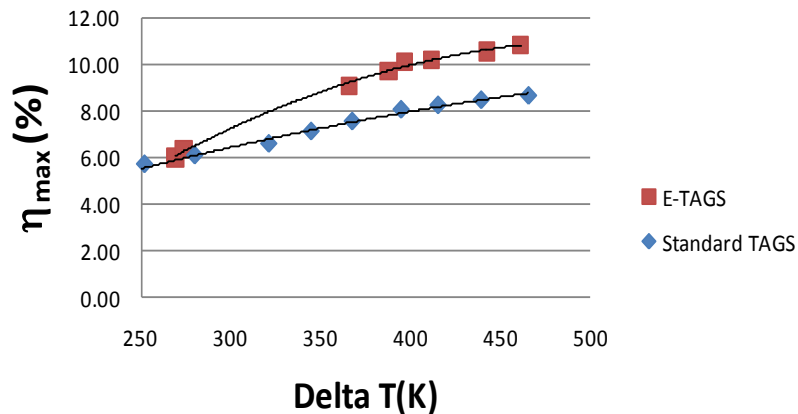

Figure 2. Improved TE device performance for enhanced TAGS-85 compared with conventional TAGS-85 materials.

- **Significant progress in Enhanced p-TAGS/conventional n-PbTe device over conventional p-TAGS/n-PbTe TE power generation** (RTI & Ames)

- **ZT~1.8 was established at 800K in mid-temperature, multi-valley degenerate p-PbTe** (Caltech)

- First set of nano-Bi_2Te_3 -E-TAGS/PbTe cascade power devices showed promising results with **T_{hot}~500C and T_{cold}~5C** (RTI)

- Doping tuning, new compositions, including novel Zintl-phase compounds, and $La_{3-x}Te_4$ for high-temp (JPL)

- JPL hi-temp couples, using baseline materials, for T_{hot}~500C to ~1000C integrated with nano-Bi_2Te_3 -E-TAGS/PbTe cascade

- Band offsets measured in PbTe-GeTe system (Delaware)

- Framework of mean free path (MFP) *distributions* as a theoretical tool for understanding thermal conductivity in bulk and nanostructures and modeling of key NMP materials (UCR)

Discussion of key RTI achievements

Delta-doped N-type Bi$_2$Te$_{3-x}$Se$_x$:Se

- "Delta-doping," is a thin film growth technique used to produce thin layers with high dopant concentration, that has allowed us to maintain high carrier mobility, while increasing the carrier concentration, and lowering the k$_L$ by increasing local anharmonicity. Growth of delta-doped N-type Bi$_2$Te$_{3-x}$Se$_x$:Se samples showed that the lattice thermal conductivity can be reduced while the power factor is enhanced. It was observed for a given period of ~60Å for delta-doping, that both power factor increases and lattice thermal conductivity decreases with increased Se delta-doping time. ZT (measured by Harman method, which includes the effect of two contacts to materials and so the "materials" ZT is estimated conservatively) was found to increase to >1.0 for a delta doping period of 30Å, significantly higher than that observed for 60Å periods.

- Optimization of delta-doped N-type Bi$_2$Te$_{3-x}$Se$_x$:Se superlattices for improved electrical contacts demonstrated that ZT ~ 2 can be achieved. The improved electrical contacts were based on Ag at the interface layer to the thermoelectric material, and an optimized annealing cycle of the contacts. Previous work on Ag-based annealed contacts on non-delta doped N-type SL samples did not improve the ZT beyond 0.5; so, the observed ZT values in the range of 1.3 to as much as ~2 were highly encouraging. In addition, it was observed that the optimum period, where ZT was maximized in the initial study, appeared to be around ~20Å, ~30Å with an unusual minimum in ZT in between these periods. More understanding of the enhanced ZT as a function of period of delta-doping is needed in future studies beyond NMP. Again we note that the ZT measured by Harman method includes the effect of two contacts to materials, and so the "materials" ZT is estimated conservatively; this should be significantly higher than 2. In any case, the observed ZT>2 data on several N-type delta-doped Bi$_2$Te$_{3-x}$Se$_x$:Se superlattices was encouraging to meet the NMP objectives for low-temperature thin-films.

- RTI also explored the growth of the N-type Bi$_2$Te$_{3-x}$Se$_x$ materials on 6-degree-offset, mis-oriented GaAs substrates, compared to standard 2-degree-off substrates, in order to obtain smoother morphology for thicker epi films (>6 μm). Interestingly, we observed a ZT ~0.9 by Harman method in non-delta-doped n-type SL on such substrates, which is x1.5 better than conventional SL material on standard 2-degree-off substrates. Also, this ZT was achieved with a power factor of only 21 μw/cm-K^2 compared to delta-doped materials which have power factors ~70 to as much as 100 μw/cm-K^2. This illustrated that significant thermal conductivity reduction can be obtained by "smooth" growth of conventional SL films.

- In collaboration with *Purdue University*, *RTI* investigated coherent optical phonon properties in delta-doped N-type Bi$_2$Te$_{3-x}$Se$_x$:Se superlattices. The delta-doping increases the optical phonon scattering rate, as measured by Purdue University's femtosecond photo-reflectance set-up. Coherent phonons are excited via displacive excitation or impulsive stimulated Raman scattering. Coherent phonons vibrate at sub-picosecond time scale, and can be detected using femtosecond laser pulses. Coherent phonon measurements provide information about electron-phonon scattering and phonon-phonon scattering, and can be used to understand the energy transfer process in thermoelectric materials. The acoustic phonon scattering rates are expected to be enhanced in delta-doped superlattices, compared to that seen for optical phonons here, thus lowering lattice thermal conductivities. Along with enhanced carrier mobilities, these are

conistent with the observed enhanced ZT in the delta-doped superlattices in the early studies. RTI 3-ω data on delta-doped N-type superlattices show ultra-low lattice thermal conductivities as well.

- The study of delta doping to control the carrier levels in the delta-doped N-type $Bi_2Te_{3-x}Se_x$:Se superlattice films showed that carrier levels can be controlled precisely by adjusting the growth time, for a given delta-doping time. The in-plane power factor also showed dramatic improvement, by a factor of nearly 14 which is unprecedented by any standard, by controlling the growth time. The exceptionally high power factors were maintained at the smallest periods investigated, showing that any drop in carrier mobility is offset by enhanced Seebeck coefficient. A systematic study of ZT at 300K- measured by Harman method that directly measures ZT as opposed to from calculating based on individual material properties that make up ZT- as a function of delta doping period and carrier concentration in the film was carried out to further understand the mechanisms of ZT enhancement. A quantum-mechanical modeling of mini-band transport due to delta doping as well as thermal conductivity measurements are in progress. These delta-doped N-type superlattices (ZT~2.4 at 300K) along with our well-understood and characterized p-type Bi_2Te_3/Sb_2Te_3 superlattices (ZT~2.4 at 300K to 2.9 at 400K) will position us well for making p-n device couples for low-temperature stage of a 3-stage power conversion cascade device.

- Final optimization of the delta-doped N-type Bi2Te3-xSex:Se superlattices resulted in a ZT ~ 2 to 2.4 at 27°C in N-type optimized Delta-doped Superlattices (DDSL) in Bi2Te3-xSe$_x$ through the aforementioned enhancement in power factor and reduced lattice thermal conductivity.

New MOCVD reactor

- A new MOCVD reactor was acquired and brought online to grow III-V materials for mid and high-temp stages in support of the NMP program. Using the new MOCVD reactor RTI successfully grew III-V materials for mid and high-temp stages – in particular, InAs and GaSb on GaAs substrates. We obtained specular 2-di films of InAs on GaAs as well as InAs/GaSb multi-layer structures on GaAs substrates. It is noteworthy that we successfully produced a novel "*holy*" InAs structures on GaAs substrates. These "holy" InAs structures are complementary to well-observed and studied InAs nano-dots on GaAs, in the sense that the InAs film is characterized by sub-micron to hundred-nm-scale holes when grown on GaAs. Thus there is a continuous network of InAs structures, thereby avoiding quantum-confinement effects, but at the same time nanoscale to mesoscale InAs structures to lower lattice thermal conductivity, in addition to the anticipated acoustic-mismatch-related thermal conductivity reduction from InAs/GaAs interfaces. We were able to grow a GaAs smoothing layer on top of the InAs holy structures, and then repeat the growth of the InAs holy structures. The long-term vision is to create GaAs/h-InAs/GaAs/h-InAs/GaAs (where h-InAs stands for holy InAs) multilayer structures and eventually superlattices – thereby achieve a desirable high-temperature (with bandgap in between InAs and GaAs) nanoscale thin-film.

- Verification of the growth of 1nm/6nm GaSb/InAs superalttices was confirmed by Transmission Electron Microscopy. Detailed Kronig-Penny (K-P)) modeling of electron transport through these superlattices suggests an estimated e-h transition energy or effective bandgap of 0.28 eV,

suggestive of use for mid-temperature applications. K-P modeling also indicated that electron transport through the thickness of the superlattices would be desirable in a mini-band formation, implying in-plane power factor would be comparable to cross-plane value. Several GaSb/InAs superlattices samples were prepared and characterized for in-plane power factor, with optimal samples characterized by power factors as high as 30.4 μW/cm-K^2 at 300K. *RTI* requested *UCR* to carry out modeling of cross-plane thermal transport in GaSb/InAs SL to see what thermal conductivity reduction can be obtained in the material system. This modeling suggested that GaSb/InAs SL structures with thermal conductivity at 300K that could approach values as low as 2 W/m-K (for non-specular scattering) to as high as 21 W/m-K (for specular scattering) for a 10-nm period. 3-ω measurements on the more optimal 7-nm period GaSb/InAs superlattices structures indicated a thermal conductivity of 12.2 W/m-K, about the average between specular and non-specular scattering modes. This indicates a ZT of only ~0.08 at 300K, comparable to ErAs-Nano:InGaAs/InAlAs superlattices being developed by Shakouri et al. at UCSC at 300K, but is expected to increase significantly to >1 at mid-temperature ranges (>700K). Future follow-on work to improve the power factor in GaSb/InAs SL by optimal doping is needed, as well as to develop approaches to lower the thermal conductivity closer to the 2 W/m-K range, first at 300K, and eventually for achieving ZT > 2 at elevated mid-temperatures.

Nano-dot superlattice (NDSL) in Si/Ge

- As part of the NMP project, RTI began work on understanding how to control the nano-dot formation to lay the ground work for reliable high-temperature **nano-dot superlattice (NDSL) in Si/Ge** and other material systems. In collaboration with *Purdue University*, *we* completed an initial investigation of **coherent optical phonon properties in Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices**, which will serve as a "model" nanoscale system – due to its well-established phonon-blocking, electron-transmitting properties leading to a ZT of 2.4 at 300K (*Nature* 2001). It was found that the scattering rate (i.e., inverse of lifetime) of optical phonons in a superlattice is significantly higher than that of the corresponding values in Bi$_2$Te$_3$ and Sb$_2$Te$_3$; this represented the *first* direct measurement of coherent phonon lifetime reduction in superlattice structures, consistent with the observed reduction in thermal conductivity in superlattices. The work was published in Applied Physics Letters.

- Ge nano-dots, with diameter of ~50 to 60 nm, a height of 2 to 5 nm and a density of ~5 to 10e19/cm^2, were chosen for initial thermoelectric property measurements. Ge nano-dots were uniformly capped and planarized with Si and stacked again with Ge nano-dot and another Si planarizing or smoothing layer. Such stacked Si/Ge NDSL was shown to have thermal conductivity values in the range of 2.5 W/m-K for periods of 5 nm. Several such n-type Si/Ge NDSL samples were grown and characterized for electrical power factor. Unlike 2-D Si/Ge superlattices, these NDSL structures were expected to be electrically isotropic. The highest power factor measured was about 111 μW/cm-K^2 at 300K in a 5 nm Ge NDSL, consisting of 2nm Ge and 3 nm Si. This was measured using a differential equivalent circuit model for measured electrical transport. Using, a similar differential equivalent circuit model, pure Ge films showed power factors of 45μW/cm-K^2, which is comparable to bulk Ge. The 5 nm period n-type Si/Ge NDSL, with such a high power factor, indicated a 300K ZT as high as 1.34. This ZT would increase significantly at higher temperatures, such as 450C to 750C targeted for the high-temperatures. This ZT result is highly promising and is likely to have a significant impact in thicker NDSL materials for devices as well as p-type component materials. The p-type Si/Ge NDSL materials were found to behave comparably to the n-type materials mentioned above.

- Despite the promising results, we felt that these materials would not likely offer a near-term solution for robust for high-temperature power conversion to 800C, compared with bulk materials, to achieve the 30% NMP conversion efficiency goals.

Coherent optical phonon properties in Bi_2Te_3/Sb_2Te_3 superlattices

- In collaboration with *Purdue University*, *RTI* completed an initial investigation of **coherent optical phonon properties in Bi_2Te_3/Sb_2Te_3 superlattices**, which serves as a "model" nanoscale system – due to its well-established phonon-blocking, electron-transmitting properties leading to a ZT of 2.4 at 300K (*Nature* 2001). It was observed that the phonon amplitude and mode signatures are indicative of weak electron-phonon coupling in Bi_2Te_3, the minority component of the Bi_2Te_3/Sb_2Te_3 superlattice, thereby increasing the scattering rate of optical phonons (inverse of lifetime) in a superlattice - significantly higher than those in Bi_2Te_3 and Sb_2Te_3. This model suggests the possibility to obtain a significant increase in scattering rates in the delta-doped N-type $Bi_2Te_{3-x}Se_x$:Se superlattices – again, due to the minority component of the delta-doped layer in the layered $Bi_2Te_{3-x}Se_x$ material. Measurements indicated that the scattering rate of optical phonons increases with both delta-doping and shorter period of delta-doping.

Mid-temperature PbTe/GeTe nanoscale thin-films

- Based on published phase diagrams, GeTe exhibits a miscibility gap with PbTe, so that a solid solution is not expected near the middle of the composition range. Hence, either good 2-D layered structures or nano-dot superlattice (NDSL) structures were predicted to exhibit promising thermoelectric properties. Consequently, RTI initiated work on **mid-temperature PbTe/GeTe nanoscale thin-films**. The initial plan was to compare superlattice films to PbTe, GeTe and alloy films to look for enhanced mobility, lower thermal conductivity and enhanced power factor. Transmission measurements confirmed the bandgaps of PbTe and GeTe to be 0.32eV and 0.31eV, respectively, thus indicating the likelihood for very little conduction or valence band offsets in a PbTe/GeTe SL system. The 0.31 eV bandgap of GeTe was considered nearly ideal for a crystalline film, as higher bandgaps would indicate an amorphous character. This, plus the fact that the lattice constants of PbTe and GeTe are 0.645 nm and 0.600 nm respectively, gave this superlattice material system a high degree of potential success for enhanced ZT through phonon-blocking/electron transmission characteristics seen in the model "Bi_2Te_3/Sb_2Te_3" superlattice system.

- The measured power factor values resulting from the first round of film growth runs achieved values of ~20 μw/cm-K^2 in SL films compared with ~35 μw/cm-K^2 seen in single-layer GeTe films. The lower power factor would diminish any advantages from lattice thermal conductivity reduction with superlattices, and thus not likely to improve ZT significantly. Hence the goal for the second round of optimization was to obtain power factor in SL structures that are comparable to pure GeTe films. It was believed that the lower power factor in the GeTe/PbTe SL structure resulted from the compensation of n-type PbTe in a strongly p-type GeTe. Therefore, the goal was to minimize the PbTe component in the GeTe/PbTe SL structure. *RTI* requested *UCR* to carry out modeling of cross-plane thermal transport in GeTe/PbTe SL to see if thermal conductivity reduction could be obtained with an ultra-thin PbTe component layer. The UCR modeling predicted that GeTe/PbTe SL structures would have a thermal conductivity at 300K that approaching 0.4 W/m-K (for non-specular scattering) to 1.3 W/m-K (specular scattering). With an average thermal conductivity of 0.85 W/m-K, the estimated ZT at 300K would reach 1.4

at 300K! This ZT would increase significantly at higher temperatures, such as 150C to 450C, targeted for these mid-temperature films. The direct measurement of thermal conductivity in these superlattice films involved contact development and thermoelectric element fabrication.

- Continued study of mid-temperature PbTe/GeTe superlattice thin-films determined that a p-type PbTe/GeTe, 1 nm/10 nm superlattice, is capable of achieving a power factor as high as ~40 μW/cm-K^2. This was a significant achievement, in spite of the potential n-type compensation of PbTe within the p-type superlattice. The superlattice quality of the 1nm/10nm PbTe/GeTe structure was confirmed by both XRD satellites and TEM imaging. The TEM showed a hybrid PbTe/GeTe 2-dimensional SL interspersed with 3-dimensional PbTe-rich nano dots. Thus, these structures are likely to exhibit a significant reduction in thermal conductivity from both a superlattice effect, creating specular scattering and any backscattering of phonons, as well as non-specular or diffused scattering. The high a power factor, plus the ability to lower thermal conductivity significantly through a superlattice approach, enables a high ZT. Temperature dependent measurements were carried out with these materials. For the P-type PbTe/GeTe SL, the fully-optimized ZT is expected to exceed 2 between 177 and 327°C due to thermal conductivity reduction and further improvement of power factor at optimal, elevated temperatures.

Nano-bulk Thermoelectric Materials and Devices

- RTI, in collaboration with NCSU, developed an approach to synthesize bulk n- and p-type chalcogenide alloy materials by high-energy mechanical ball milling and/or cryogenic ball-milling of elementary powders with subsequent densification by high-pressure uniaxial hot-pressing. We studied the influence of processing variables such as temperature, compaction time and pressure on transport properties of the resulting sintered materials. X-ray diffraction was employed in order to estimate grain size after processing. P-type Nano-$Bi_2Te_{3-x}Sb_x$ bulk alloys with ultra-low thermal conductivity has achieved a ZT of 1.7 between 27°C and 100°C at RTI**.** Work was also carried out to apply the methods developed for p-type nano-bulk materials to corresponding n-type nano-bulk $Bi_2Te_{3-x}Se_x$ materials. We demonstrated that these bulk materials exhibit a unique mixture of nanoscale features that leads to enhanced Seebeck coefficient and reduced lattice thermal conductivity, thereby achieving an *average* ZT of ~1.26 and ~1.7 in the 27 ºC to 100 ºC range for the n-type and p-type Bi_2Te_3-based materials, respectively. These new nanostructured bulk materials will serve as a potential foundation for future thermoelectric power generation applications.

- *NCSU* and *RTI* collaborated on optimization of both p- and n-type Bi_2Te_3-based nano-materials; this involved room temperature and/or cryogenic ball-milling followed by mechanical sintering. XRD was used to obtain grain sizes prior to compaction. In addition, RTI has obtained 6.1% conversion efficiency for the p-n nano-bulk couple made from these materials, compared to ~5.35% obtained for state-of-the-art Ferrotec conventional Bi2Te3-alloy p-n couples. (Also discussed in NCSU summary)

- Heat-to-electrical single-stage power conversion devices fabricated using the nanostructured chalcogenide alloys were shown to demonstrate a dramatic 35% device efficiency improvement compared to similar devices using state-of-the-art thermoelectric $(Bi,Sb)_2(Te,Se)_3$ materials. A

typical n- p- device "couple" and a corresponding schematic diagram are shown in Figure 3, below.
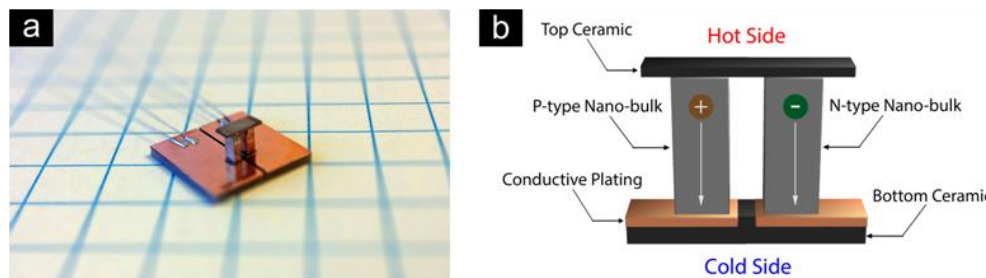

Figure 3. Photograph of a typical n- p- device "couple" (left) and a corresponding schematic diagram (right).

With these nanostructured chalcogenide alloy couples, *peak* single-stage device efficiency was between (7.2±0.25)% and (7.9±0.25)% with an average of (7.5±0.25)% at a temperature difference ($\Delta T = T_h - T_c$) of 300 °C (see Figure 4, below). Commercial off-the-shelf (COTS) chalcogenide-alloy devices, on the other hand, exhibit a peak efficiency of (5.6±0.25)% at $\Delta T \sim 225$ °C. The devices fabricated from our nanostructured materials developed during the NMP project exhibit peak efficiency at higher temperatures ($\Delta T \sim 300$ ºC) than the COTS devices ($\Delta T \sim 225$ °C) because the latter employs materials produced by conventional melt-growth method, and the ZT typically peaks at lower temperature (85 and 25 °C for p and n-type), which also explains the fact that the efficiencies become comparable at smaller ΔT regime. Previous work on solar thermoelectric generators utilizing nanostructured chalcogenide alloys achieved 5.2% at $\Delta T = 200$ °C. For the same ΔT, our devices exhibited an efficiency of (6.1±0.25)%. The >17% improvement directly reflects the higher average ZT values. High temperature performance is particularly attractive for applications in exhaust waste-heat recovery, a likely technology transition and insertion area for DoD applications.
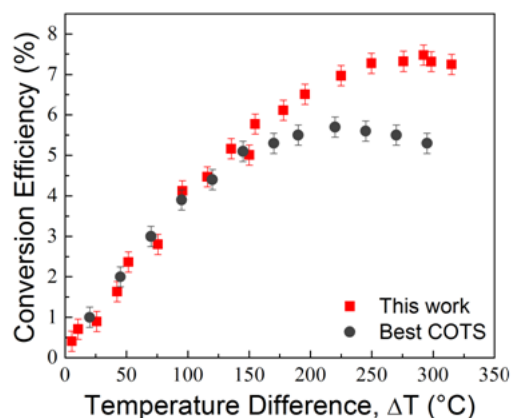

Figure 4. Comparison of single-stage power conversion device performance of the nanostructured chalcogenide alloys developed under the NMP program, compared with similar devices prepared from state-of-the-art thermoelectric $(Bi,Sb)_2(Te,Se)_3$ materials, showing a 35% improvement in heat-to-electrical conversion efficiency.

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- A major advancement, approaching the overall project goal of 30% heat-to-electrical conversion efficiency, was achieved through the development of advanced, three-stage cascade device technology. During the course of NMP, improvements in bulk materials (discussed above for the nano-bulk Bi_2Te_3-based compositions) lead to continual improvements in device efficiency. In addition, we implemented an area aspect ratio optimization process to account for unequal heat flow down the individual legs. The resulting 3-stage device was based on nano-bulk Bi_2Te_3-based materials for the lower (colder) stage, PbTe/e-TAGS for the mid-stage, and half-Heusler alloys for the hot stage, as shown in Figure 5, below.
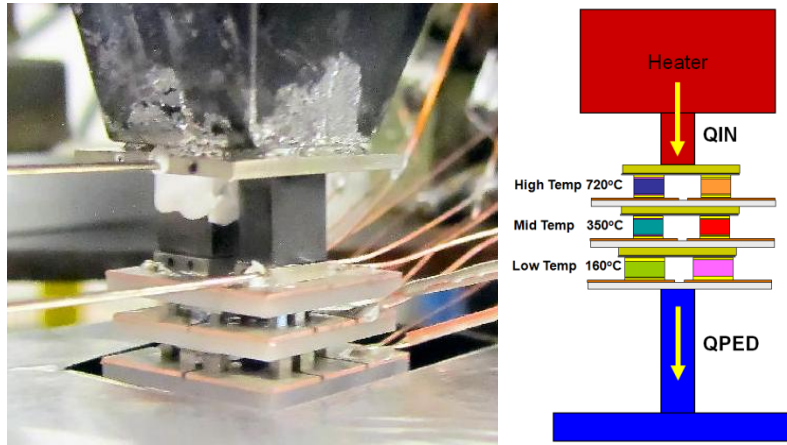

Figure 5. Photo of 3-stage device based on nano-bulk Bi_2Te_3-based materials for the lower (colder) stage, PbTe/e-TAGS for the mid-stage, and half-Heusler alloys for the hot stage (left); schematic diagram of the device configuration and TE leg temperatures (right).

The conversion efficiency of this material/device configuration reached a world-record 26% in multiple tests, and on multiple devices (see Figure 6, below).
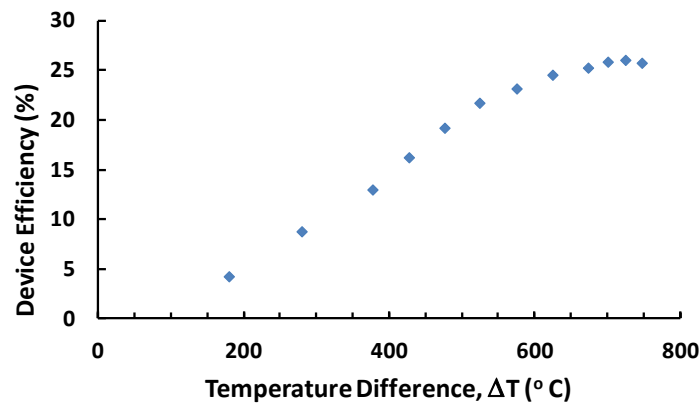

Figure 6. Measured heat-to-electrical conversion efficiency of optimized 3-stage TE device, showing a peak efficiency of 26%, a world record, for a ΔT of 750°C.

- Through the NMP program, we demonstrated that an optimal hot pressing pressure is required for maximum thermoelectric power factor in different n-type Bi(Se)Te alloys, modulated mainly by the variations in the carrier concentration and thus the Seebeck coefficient. This

phenomenon is attributed to the increases in the amount of positively charged antisite defects as the pressure increases to a point where their contributions are canceled out by other negatively charged antisite defects. Modifications of the energy gap resulting from the lattice distortions at high pressure also likely play a role.

- For highlights on additional bulk materials, please refer to summaries by Ames Laboratory, JPL, and UTRC in the "subcontractor" section, below.

Other Focus Areas – including NMP "add-on"

- During the project's final "add-on" period, a significant amount of progress was realized in the area of growth and characterization of the n-type GaSb/InAs superlattices, with the demonstration of 1nm/6nm GaSb/InAs superalttices by Transmission Electron Microscopy. Several GaSb/InAs superlattices samples were prepared and characterized for in-plane power factor, with optimal samples indicating power factor as high as 30.4 μW/cm-K^2 at 300K. For the N-type GaSb/InAs SL, a ZT_{ave}>1.4 between 177 and 377°C was estimated as a result of thermal conductivity reduction and improvement in power factor at optimal, elevated temperatures. Additional follow-on work is recommended to develop viable approaches for reducing the thermal conductivity close to 2 W/m-K, in order to achieve ZT > 2 at elevated mid-temperatures.

  a. RTI achieved extraordinarily low thermal conductivity (0.03 W/m-K @ 2 nm thick) in *crystalline* Bi2Te3 thin films (partially supported by DARPA MESO program). (Ultra-thin Bi_2Te_3 films have shown potential for ZT in the range of 5 to possibly as high as ~10 at 300K.) Results were experimentally determined by two independent measurement techniques, as shown in Figure 7, below.
     i. 3ω – Measured at RTI
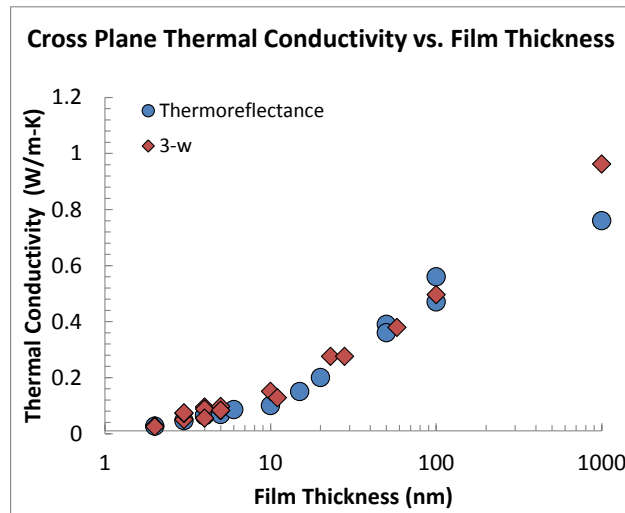   ii. Thermoreflectance - Measured at Purdue

Figure 7. Cross-plane thermal conductivity vs. film thickness for ultra-thin crystalline Bi2Te3 films.

- Quantum-confinement effects were also observed for the first time in one of the most important TE materials, Bi_2Te_3, through a GaAs-Bi_2Te_3-air heterostructure.

- RTI successfully developed methods for controlled synthesis of 2 nm to 58 nm films at a very precisely-regulated deposition rate of 0.04 nm/sec.

- RTI and NCSU identified Ga_2Te_3 interfacial layer via STEM measurements. This Ga_2Te_3 layer enables sharp interfaces and the epitaxial growth of Bi2Te3 on GaAs substrates. (Published in: APPLIED PHYSICS LETTERS **102**, 081601 (2013) (see Figure 8, below).
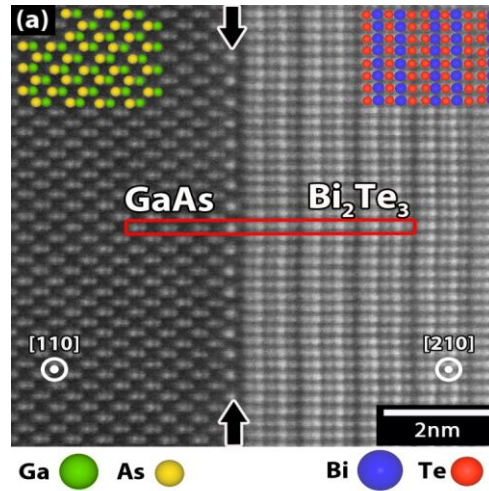

Figure 8. TEM image of atomic layer interface between Bi_2Te_3 and GaAs, showing formation of a thin Ga_2Te_3 interfacial layer that enables epitaxial growth of Bi_2Te_3 on GaAs.

- RTI measured as-deposited power factors of Bi2Te3 thin films as a function of film thickness and found the maximum power factor to be ~30 µW/cm-K^2 at a thickness of 10 nm, as shown in Figure 9, below.
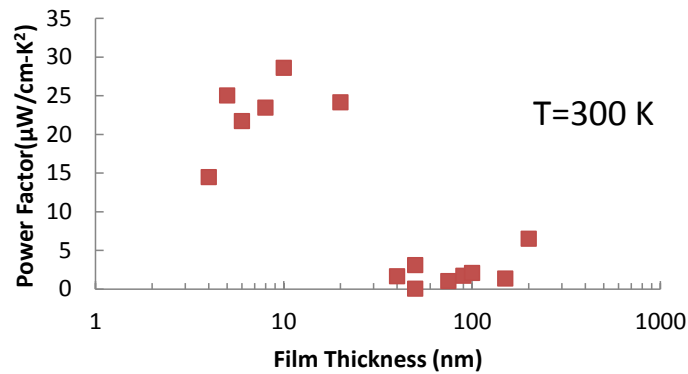

Figure 9. As-deposited power factor of Bi2Te3 thin films as a function of film thickness.

- As shown in Figure 10, below, RTI subsequently achieved an improved power factor in *5 nm thick* Bi2Te3 thin avoid evaporation of the film.
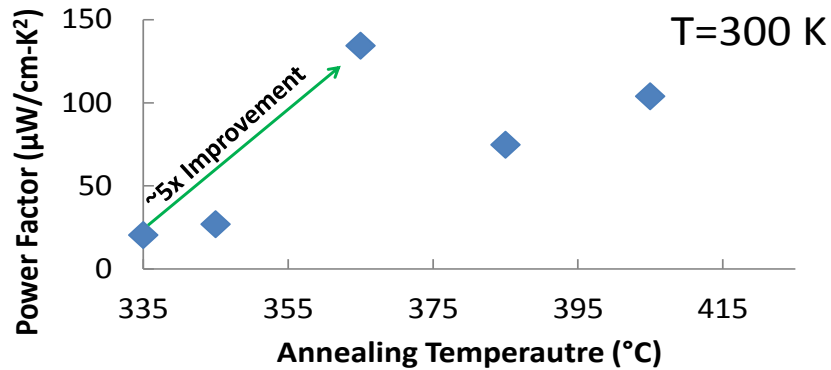

Figure 10. Measured power factor in 5 nm thick Bi2Te3 thin films prepared using an in-situ annealing process with a Te-overpressure.

- Given the impressive power factor (130 μW/cm-K^2) and low measured cross-plane thermal conductivities, the potential for development of future, follow-on high ZT material is highly promising, as shown in Figure 11.   ZT > 2.0 appears achievable assuming the modest in-plane thermal conductivity of 2 W/m-K.
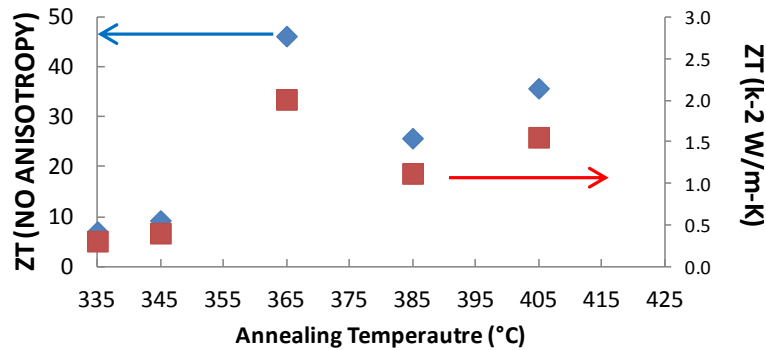
Figure 11. Estimated ZT vs. annealing temperature for 5 nm thick Bi2Te3 thin films.

- RTI also developed high power factor, high Sb-content (BiSb)$_2$Te$_3$ thin films
   a.   We note high power factor >140 μW/cm-K2 for thin Bi$_{0.1}$Sb$_{1.9}$Te$_3$ thin films for thickness ~ 100 nm.
   b.   In the final year of the NMP program, we developed processes to grow similar material at a faster growth (more than 2x) rate in order to achieve thicker films (~1 μm) that could be suitable for future device fabrication. Note: The power factor of typical p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice films is ~100 μW/cm-K^2

Sample	Program	Growth Rate (nm/min)	Resistivity (Ω-cm)	Mobility (cm^2/V-s)	Carriers (cm^{-3})	Seebeck (μV/K)	Power Factor (μW/cm-K^2)
7-4474	MESO	4.5	4.99E-04	480	2.61E+19	258	133
7-4483	NMP	***11.0***	6.17E-04	351	2.88E+18	301	147

- RTI established growth of ~30 μm thick p-type Bi_2Te_3/Sb_2Te_3 superlattice and n-type $Bi_2Te_{3-x}Se_x$ Δ-doped alloys. To achieve the thicker films a 3-step growth process was developed wherein the growth was interrupted approximately every 10 μm to confirm the surface morphology was acceptable, and the process was then re-initiated on the same surface. Below is a table summarizing the properties of the as-grown thin films. These thicker films will reduce parasitic losses associated with thin film device processing and improve device performance.

Sample	Material	Thickness (μm)	Resistivity (Ω-cm)	Mobility (cm^2/V-s)	Carriers (cm^{-3})	Seebeck (μV/K)	Power Factor (μW/cm-K^2)
7-4470	p-type Bi_2Te_3/Sb_2Te_3 SL	***27.5***	7.34E-04	382	2.23E+19	285	111
7-4465	n-type $Bi_2Te_{3-x}Se_x$ Δ-doped	***32.4***	1.40E-03	225	1.98E+19	-293	61

- RTI also collaborated with General Dynamics Land Systems (GDLS) on an ARL-funded program to evaluate TE for waste heat recovery. RTI, in collaboration with GDLS and Creare, demonstrated power levels of 80-Watts in fractional-scale, proof-of-concept tests, and RTI/GDLS have been evaluating the next phase towards a 5-kW demo and eventually to a final system of 25 to 50-kW.   The advanced TE materials on NMP (especially below 450C) and their modules are expected to fit in this roadmap.

Subcontractor Achievements

JPL

JPL's initial focus was on optimizing low thermal conductivity rare earth compounds to achieve ZT values of 1.5 to 2.0 in the 800 to 1050 K temperature range. The current baseline materials developed for long life NASA applications, n-type $La_{3-x}Te_4$ and p-type $Yb_{14}MnSb_{11}$, have peak ZT values in the 1.3-1.5 range at 1275 K, close to 1.0 at 1050K and about 0.8 at 900 K. Significant (i.e., > 50%) improvements in power factor and reductions in lattice thermal conductivity were necessary to achieve the DARPA NMP goals. Tuning of the electrical properties to maximize ZT values in the targeted temperature range required a significant reduction in carrier concentration. Such reductions, from 1.2×10^{21} h/cm^3 down to the 10^{19} h/cm^3 range, were achieved in Al-rich $Yb_{14}Mn_{1-y}Al_ySb_{11}$ ($0.7 \leq y \leq 1.0$) samples synthesized by high energy ball milling. This now enables the full impact of lattice thermal conductivity reductions onto peak ZT values, which are predicted to reach 1.5 or higher at 900 K for carrier concentrations near 1×10^{20} h/cm^3 for the plot of ZT versus hole concentration and for 0, 25 and 50% reductions in lattice thermal conductivity. The reduction in lattice thermal conductivity were sought through three different synthetic routes: preparation and characterization of new 14-1-11 bulk compositions, nanostructuring through in-situ formation of nanoscale conductive precipitates within the 14-1-11 matrix, and nanocomposites that include nanoscale inert scattering inclusions. Synthetic techniques for all three approaches were demonstrated for the nanostructuring approaches using the baseline semi-metallic $Yb_{14}MnSb_{11}$ composition. Similar results were also achieved in the n-type $La_{3-x}Te_4$ system with both metallic (Ni) and insulating (SiC) nanoscale inclusions. Activities also focused on achieving precipitate and inclusion sizes below 100 nm, and ensuring a homogeneous distribution throughout the host matrix. In spite of poor control over size and distribution, the inclusions have a low impact on electrical properties in the 14-1-11 Zintls, which is key to maximizing gains in lattice thermal conductivity reductions. Hence, the prerequisites in terms of reducing hole concentration and introducing nanoscale inclusions for lower lattice thermal conductivity were accomplished through the development of suitable synthetic routes.

Ames Laboratory

Ames Lab investigated nano-structured PbTe, to reduce lattice thermal conductivity. The approach was to use the binary compound GeTe, which is known to form a spinodal region with PbTe, as a second phase in PbTe. The effort was driven by the constraint that the inclusions should be coherent with the matrix to minimize scattering of charge carriers, but possess different elastic modulus and lattice constant to introduce strain the matrix, which was expected to scatter intermediate wavelength phonons. X-ray diffraction showed evidence of two distinct phases in 40% and 50% GeTe samples.

The addition of GeTe was indeed shown to facilitate the formation of nanoscale precipitates in PbTe, as seen in the inset of Figure 12. The figure also shows the effect of GeTe additions on the Seebeck coefficient. In order to extend these effects to obtain superior n-type PbTe, recent efforts have been focused on additions of PbI_2 to PbTe+GeTe. In our initial effort, we were successful in producing a PbTe+10 mol. % GeTe nanocomposite with a 300K Seebeck coefficient of -294 μV/°C.
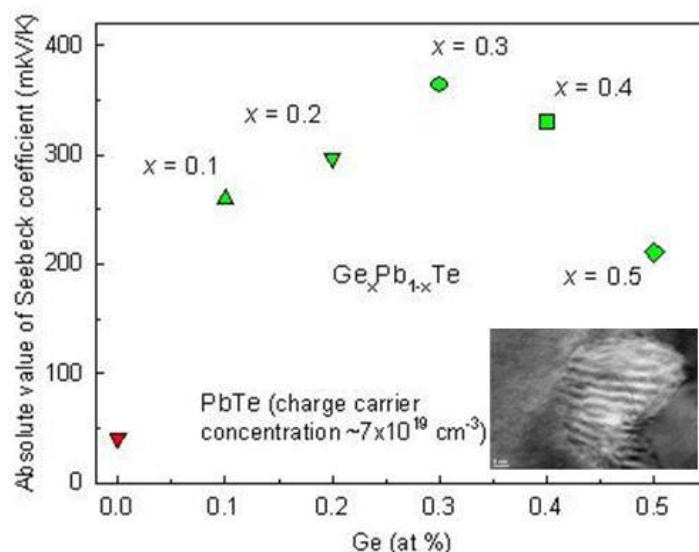

Figure 12. The effect of GeTe additions to PbTe on the Seebeck coefficient. GeTe is added to nanostructure the material (inset) for thermal conductivity reduction.

The encouraging observation of coherent nano-inclusions in PbTe with GeTe addition, combined with very high Seebeck coefficient values of 250 to 350 microV/K and low thermal conductivity values of ~ 8 mW/cm-K, led efforts to introduce dopants into this system in order to optimize the electrical conductivity. Samples of PbTe + 10, 20, 30, 40, and 50 mole percent GeTe were synthesized by melt processing in which 0.1% and 0.2% PbI_2 were added to the initial charge. Unfortunately, work on this system was terminated before full characterization of TE properties could be measured.

In addition, Ames investigated the introduction of f-level resonant states near Fermi Energy in TAGS-85 [$(AgSbTe_2)_{15}(GeTe)_{85}$] for the enhancement of Seebeck coefficient.   TAGS-85 is a well-known thermoelectric material based on germanium monotelluride that exhibits a second-order displacive transformation from a high-temperature cubic to a low-temperature rhombohedral polymorph. TAGS

has historically exhibited poor uniformity, with cast materials exhibiting segregation of Ge and also Ag-Te, leading to a three-phase microstructure. The presence of undesirable secondary phases is observed not only in the cast ingots, but also in hot pressed compacts as well. In general, homogeneous materials exhibit higher ZT values than inhomogeneous structures, because of the scattering effects associated with interfaces and local deviations from the optimal composition.

This program involved addition of small amounts of the rare earth elements Ce and Yb to TAGS-85, and has demonstrated a reproducible 25 to 30 percent increase in ZT at 700K in materials obtained by solidification from the melt. Analysis by x-ray diffraction of the chemically-modified alloy suggests a partial stabilization of the high-temperature cubic polymorph. ^{125}Te NMR studies confirmed the incorporation of rare earth cations into the GeTe-based lattice. Solid state synthesis was successfully applied to the processing of rare-earth-doped TAGS-85 and has resulted in a further increase in ZT beyond the levels initially observed in melt-solidified materials.

Despite the chemical inhomogeneity, "neat" TAGS-85 exhibits a maximum ZT of ~ 1.2 to 1.3, which was increased to 1.8 for mid-temperature applications (~700K) with the addition of 1% divalent rare earths, Yb and Ce as a result of this program. As part of a broader effort to achieve higher ZT values in TAGS with rare earth additions, we have investigated process modifications to eliminate phase segregation and achieve a more uniform structure. One variable that has been recently investigated is the maximum temperature during melt processing, which had been established as 825°C by early processing work performed in the 1970's. We have prepared TAGS-85 ingots in which the maximum temperature was increased to 900°C and 1000°C, in order to achieve complete dissolution of all constituents in the melt. Another processing variable that was investigated is the effect of long-term heat treatments to facilitate solid-state dissolution of the second phase inclusions. We also examined TAGS-85 with addition of Gd, a rare earth element possessing a higher magnetic moment than either Ce or Yb, in order to determine the extent to which magnetic scattering is contributing to the increase in ZT. This was necessary in order to understand the underlying physics behind the observed performance enhancement.

The temperature dependencies of the Seebeck coefficient, a, electrical conductivity, s, power factor (a^2s), and thermal conductivity, κ, were measured in samples containing rare earth additions. It was seen that the electrical conductivity remains essentially unchanged in the samples containing 1%Ce or 1%Yb, while the Seebeck coefficient is increased by ~13% at 300 K and by ~16% at 700 K. While the neat TAGS-85 at 700 K reaches a maximum power factor of 27 μW·cm^{-1}·K^{-2}, the rare earth-containing samples achieve a maximum power factor of 36 μW·cm^{-1}·K^{-2}. The effect of doping TAGS-85 with Ce or Yb on power factor is similar.

Although the thermal conductivity of TAGS-85 doped with Ce and Yb at 700 K is higher by 3-5% than that of neat TAGS-85, increase in Seebeck coefficient by 16% overcomes a negative effect from the thermal conductivity and *ZT* reaches 1.8 (note that *ZT* $\propto$ S^2). This is one of the highest *ZT* values reported for bulk, p-type TE materials. Two developments were particularly encouraging. The addition of Gd produces a casting that appears to possess lower porosity than previous castings. In addition, improvements in the gas handling system used to seal quartz ampoules has led to castings of baseline TAGS that likewise appear to be of lower porosity. A complementary solid-state reaction synthesis (SSRS) technique to casting was also developed for rapid, low-cost synthesis of TAGS. This method involves powder processing techniques, including solid state reaction synthesis, to produce fine grained, highly-homogeneous bulk materials.

Cal-Tech

Cal Tech initiated work on mid-temp materials, after discovering that 10 to 20 nm Zn nanoparticles remain dispersed in Zn_4Sb_3, a mid-temperature/high-temperature material. They also looked at PbTe nano composites, drawing inspiration from their work on earlier efforts involving PbTe-Sb_2Te_3 nano-composites. Cal Tech was asked to complete identification and plans for candidate materials for hi-temperature stages. Cal Tech was encouraged to bring in the expertise of JPL in producing La_3Te_4 nano-composites (hi-temp N-type) and $Yb_{14}MnSb_{11}$ (hi-temp P-type) materials. Specifically, they have provided a high-temp p-type $Yb_{14}MnSb_{11}$ roadmap and an n-type La_3Te_4 roadmap. They initiated work on high-temp materials and have reported one of the first nanocomposite in La_3Te_4 with a refractory second phase precipitate; they also examined PbTe and other dopants as the second-phase precipitate. They projected a ZT >1 to as much as 1.2 in this N-type La_3Te_4 high-temperature material. Their goal was to reduce lattice thermal conductivity in $Yb_{14}MnSb_{11}$ by composite formation. In the mid-temperature materials development, Cal Tech developed a PbTe-Ag_2Te nanocomposite, in which nano-particle/second phase are formed at ~500°C. Particles with size of 5 nm have been observed in TEM. A potential ZT in the range of 1.5 was achieved at ~ 500°C in these n-type materials, to complement advanced p-TAGS developed by Ames Lab and described above.

As part of this combined effort, JPL was able to complete the synthesis of 6 new 14-1-11 Zintl compositions derived from the baseline p-type $Yb_{14}MnSb_{11}$. Five of the six new compositions showed some amount of the desired 14-1-11 stoichiometry; these include $Yb_{14}GaSb_{11}$, $Yb_{14}InSb_11$, $Yb_{14}CdSb_{11}$, $Eu_{14}MnSb_{11}$ and $Yb_{13}NbSb_{11}$. P-type $Yb_{14}MnSb_{11}$ composites with ZT~1.4 at ~900°C using BN nano-inclusions were obtained. Even though we measure all of the thermoelectric properties, electron microscopy has shown that we have second phases present. New Zintl compositions were also attempted; Zintl phases had not been reported before and some tuning of the processing parameters were necessary before achieving synthesis of single phase samples. For further advancing n-type $La_{3-x}Te_4$, JPL synthesized nano-composites using inert inclusions such as Si3N4. YbTe inclusions into $Yb_{14}MnSb_{11}$ were also attempted. Separating the various phonon scattering mechanisms and the electronic contribution to the thermal conductivity presented a significant challenge to understanding, and further optimizing, these nanocomposites. Caltech has shown that relatively large nanometer-scale (50-200nm) Ag_2Te precipitates in PbTe can be controlled according to the equilibrium phase diagram and that these materials show intrinsic semiconductor behavior with high electrical resistivity, enabling direct measurement of the phonon thermal conductivity. Their study provided direct evidence that even relatively large, nanometer-scale microstructures reduce thermal conductivity below that of a macro-scale composite of saturated alloys with Kapitza-type interfacial thermal resistance at the same overall composition. Carrier concentration control was achieved via La doping, enabling independent control of the electronic properties and microstructure. These materials exhibited lattice thermal conductivity that approaches the theoretical minimum above ~650K, even lower than that found with small nanoparticles. Optimally La-doped *n*-type PbTe-Ag_2Te nanocomposites exhibit *zT* > 1.5 at 775 K.

North Carolina State University

Initial work at *NCSU* focused on processing of Bi_2Te_3 and Sb_2Te_3 ball-milled nano-powders using liquid-nitrogen ball-milling for nano-powders starting high purity individual component elements; they were able to produce nanocrystalline powders of 10nm average grain size with desired composition in both p-type and n-type systems. According to XRD analyses, the peak position and relative intensity were well matched with the target composition, i.e. $Bi_2Te_{2.7}Se_{0.3}$ (N-type) and $Bi_{0.4}Sb_{1.6}Te_3$ (P-type) respectively. The nano-powder consolidation indicated that good materials can be obtained from both room temperature and high temperature compaction process; while the former gives zero grain growth, the later method maintains grain size less than 30nm.

NCSU studied the influence of factors such as temperature, compaction time and pressure on properties of resulting sintered materials. NCSU optimized the processing parameters and again XRD was used to obtain grain size after processing. Bi_2Te_3 and Sb_2Te_3 ball-milled nano-powders were used for p-type materials. NCSU prepared nano-crystalline $Bi_2Te_{2.7}Se_{0.3}$ as well, by ball milling the elemental powders at either 77K or room temperature. The as-milled powders had fine nano-crystalline grain sizes which were estimated from x-ray diffraction line broadening. Samples milled at 77K had an average grain size of 8 nm. Those milled at room temperature had an average grain size of about 13 nm. The powders were consolidated by hot pressing in tungsten carbide dies under pressure of 2 GPa in an argon atmosphere at temperatures ranging from 200^oC to 410^oC, the latter near the melting point of the material.

As expected, the density of compacts increased with increasing compaction temperature and the electrical resistivity, presumably reflecting the decrease in porosity, also decreased with increasing compaction temperature. *RTI* measured all the thermoelectric properties of NCSU's nano-bulk materials including electrical resistivity by Hall-effect, Seebeck coefficient and bulk thermal conductivity by a finely calibrated q-meter. The best thermoelectric properties were observed on samples compacted around 400^oC. The best 300K ZT in p-type materials were 1.07 at 300K, 0.96 at 323K and 1.0 at 373K. The ZT values were not as high as in the UTRC nano-bulk p-type materials, described below. The p-type materials had good power factors, slightly higher than conventional bulk materials, but the thermal conductivities were not any lower than in bulk materials; thus the ZT improvement over conventional bulk p-type materials was marginal at best. On the other hand, the N-type nano-crystalline materials showed a very large ZT, as high as 1.76 at 300K, 1.66 at 323K and 1.5 at 373K. The increase in ZT is largely due to the excellent preservation of power factor in the nano-bulk materials while at the same time having a nearly factor of two smaller thermal conductivity than conventional bulk N-type materials. This represented the first observation of enhanced ZT at 300K in N-type Bi_2Te_3-based nano-bulk material by any group in the world, to our knowledge.

Thinning of the samples TEM was carried out by focused ion beam machining of these n-type samples. The samples typically had an average grain size of about 400 nm. The best p-type sample had an average grain size of about 1000 nm. No extra phases were noted in the n-type material by either x-ray diffraction or TEM, unlike the p-type material which had Te precipitates.

In addition, RTI obtained ~8% conversion efficiency for the p-n nano-bulk couple made from these materials, compared to ~5.35% obtained for state-of-the-art Ferrotec conventional Bi2Te3-alloy p-n couples.

Purdue

Purdue University contributed early on in this project to acoustic phonon transport property measurements, starting with p-type Bi_2Te_3/Sb_2Te_3 superlattices. Also, they upgraded their system to allow thermal property measurements of various materials at elevated temperatures. Purdue established a photoacoustic thermal property measurement apparatus and the corresponding numerical model for characterizing thermal properties, and used it for a number of materials including thermoelectric materials. The working temperature of this system ranges from cryogenic up to about $100^{o}C$. In addition, a laser thermal reflectance measurement system (funded by another project), was expanded from room temperature to $700^{o}C$, which was used for this NMP project. Purdue developed acoustic phonon scattering measurement methods for nano-engineered thermoelectric materials, and also samples of bulk films for comparison. Acoustic phonons are excited using a femtosecond pulse at the front of the sample surface, then measured when they are reflected back to the surface from the thin film – substrate interface using another femtosecond laser beam. The goal of these measurements was to understand the nature of phonon scattering in nano-structured thermoelectric materials, and therefore to understand the thermal conductivity reduction in these materials.

Results indicated that there is significant phonon scattering in superlattices, whereas the scattering in *bulk* film samples is insignificant. Further analyses indicated a decrease of acoustic phonon velocity, possibily resulted from folding and flattening of phonons branches. Therefore, both the interface scattering and a reduced phonon group velocity contribute to suppressing the heat transfer process. In addition, the deviations from acoustic mismatch theory have been observed. A paper was published in Appl. Phys. Lett.

UC Riverside

UC Riverside focused on the theoretical aspects of thermal conductivity of nanoscale, 2-phase material systems as well as thermal rectification approaches to enhance ZT. As part of this effort, a phonon transport model was developed for $PbTe$-Sb_2Te_3 nano-bulk material using an independent-layer analysis approach. The model predicted that the cross-plane thermal conductivity should be reduced even at larger periods; however, in-plane specularity is a key; about 70% of net thermal conductivity in a nano-bulk comes from in-plane direction while only about 30% from the cross-plane effects. Modeling of thermal rectification approaches to enhance ZT were conducted; optimization trends suggested that 2 staggered layers are better than 1, and an extended analysis to include diffuse inclusions (a year 2 milestone) shows rectification is reduced, but still present, even for zero specularity. Recall that the specularity, *p*, is defined such that smooth surfaces with *p*=1 are perfectly specular (e.g. transmission obeys an analogue of Snell's Law) while rough surfaces with *p*=0 are perfectly diffuse (e.g. transmitted phonons are scattered in many directions). UCR used a semi-classical phonon model that treats the phonons as incoherent particles (i.e., neglects wave interference effects), and the fundamental strategy was to obtain numerical solutions of the Boltzmann transport equation (BTE). A key advance is that the model accounts for the frequency dependence of the bulk phonon scattering mechanisms both in-plane and cross-plane, which had been neglected in previous BTE solutions for the cross-plane thermal conductivity.

In the area of thermal rectification, UCR validated the low-bias limit of Landauer / Bose-Einstein simulations for transport across a thin film and correctly captured the distinction between "emitted temperature" and "local equilibrium temperature" - important for these highly non-equilibrium problem. In addition, UCR provided modeling of the thermal transport in two other material systems that were investigated – $PbTe/GeTe$ (in both thin-film superlattice form at RTI and in nano-bulk form at Ames Lab) and $InAs/GaSb$ (in thin-film superlattices) both for mid-temperature applications.

UCR also carried out preliminary modeling of mean free path distributions in bulk and nanostructures. The various well-established models for frequency-dependent bulk phonon scattering (such as Holland, Klemens, and Callaway) can usually be adjusted to give excellent agreement with experiments for bulk thermal conductivity, but when these same models are applied to nanostructures the predictions no longer agree with each other. UCR concluded the program by developing a modeling framework to interpret this distinction in terms of the distributions of various mean free paths (MFPs) that contribute to thermal conductivity in bulk and nanostructures. An important initial observation was that the various established models place very different emphasis on long vs. short MFPs in bulk.

University of Delaware

University of Delaware began their contribution to this project by measuring valence band and conduction band offsets in material pairs that could be used to create novel, nanoscale thermoelectric composites. The first set of material systems considered was Bi_2Te_3 and Sb_2Te_3, the two components of the "model" p-type Bi_2Te_3/Sb_2Te_3 SL. Univ. of Delaware utilized the Stanford Linear Accelerator Center (SLAC) beam line to measure valence band energies; a significant effort was made in removing the native oxides, through appropriate chemical cleaning procedures, from the Bi_2Te_3 and Sb_2Te_3 materials; this was a joint collaborative work between *Delaware* and *RTI*. Initial results from SLAC measurements indicated that the two valence bands are close to each other and also the valence band maximums are close to the Fermi level energy, within the limits of noise in the measurements. Results on delta-doped N-type $Bi_2Te_{3-x}Se_x$:Se superlattices – the respective surfaces of a bare N-type $Bi_2Te_{3-x}Se_x$ layer and a Se-dosed layer – indicate that the valence-band energies (and hence conduction band energies, as the bandgap is not expected to be altered by Se dosing) are aligned within experimental error; this is favorable for cross-plane electron transport in the delta-doped N-type $Bi_2Te_{3-x}Se_x$:Se superlattices, potentially supporting the observation of enhanced ZT. A detailed publication of the valence-band energies in the p-type Bi_2Te_3/Sb_2Te_3 SL system was prepared.

UTRC

UTRC activities were focused primarily on 2-phase Bi2Te3-based low-temperature material systems, fabricating nanostructured bismuth telluride, antimony telluride, and bismuth telluride selenide structures initially containing nano-scale inclusions of silver telluride. Additional inclusion phases were also explored. In UTRC's initial studies with the p-Bi-Ag-Te system, Ag_2Te phase segregated to grain boundaries, and there was a need to develop process to improve 2nd phase distribution. Also, the Ag_2Te phase was larger than desired; so there was also a need for process modification in order to reduce 2nd phase size. In one particular composition (Sample#NMP-18), $(Sb_{1.5}Bi_{0.5}Te_3)_{0.975}(Ag_2Te)_{0.025}$, *UTRC* observed that the power factor (defined as $\alpha^2T\sigma$) was 0.74 W/m-K compared to 0.59 in conventional p-$Sb_{1.5}Bi_{0.5}Te_3$ alloy (Sample#NMP-17). UTRC also carried out detailed SEM electron back-scattered imaging, mapping for the Bi, Te, Sb and Ag composition profiles in the NMP-18 sample; it was observed that the matrix phase was Sb-deficient and the precipitate or second phase was Sb/Bi rich. Additional work involved consolidating pellets from mechanically milled powders. All material fabrication was targeted at producing a high ZT, p-type TE nanocomposite sample in the Sb/Ag/Bi/Te material system. The best ZT value measured was 0.48. Interestingly, this value of ZT can be obtained through either a direct solidification route or through a powder processing + hot pressing route. Based on a round of thermoelectric data, it appeared that the composite samples prepared were all in an over-doped state. The electrical resistivity value was too low (< 1 mohm-cm), while the Seebeck coefficent values were also too low, much less than the desired 180-200 μV/K. To raise the resistivity and Seebeck coefficient of these materials, another round of material fabrication was conducted in which both (i) the Ag/Sb ratio within the $AgSbTe_2$ phase, and (ii) the post-solidification heat treatment step was altered. An objective of this study was to determine if this material could yield a ZT~1.2 value at 300K, as reported earlier. The second objective was to determine if a material derived from chemical elements would give its peak ZT at a different temperature than the one derived from a commercial ingot. It was expected that the doping levels between these two materials would vary. In such a case, one might be able to "tune" the peak ZT across a wide temperature range by varying the doping levels. However, this did not yield a high ZT result; the best ZT achieved was only 0.94, not 1.2; the electrical resistivity values were higher in comparison, suggesting the need to incorporate additional dopants. However, in subsequent studies at UTRC, a ZT value of 1.35 was obtained. This higher ZT value was achieved by taking the ZT~1.2, p-type nanostructured material (from commercially procured $Sb_{1.5}Bi_{0.5}Te_3$ material) and applying a low temperature anneal to remove residual defects in the structure. Upon careful review of the thermal conductivity data and the sample measured, it was recognized that the cut sample had a surface with varying thickness. Depending upon the thickness input into the calculation for thermal diffusivity, different values were obtained which resulted in an uncertain ZT. At best the ZT value was 1.35, however in all likelihood, the sample's true ZT is somewhere between ZT ~1.2 and 1.35**.**

In order to reduce the uncertainty, new samples were fabricated and tested in the p-type nano-bulk area. A *new batch* of commercial grade, bulk (not nano-structured), p-type ingot material ($Sb_{1.5}Bi_{0.5}Te_3$) was sourced. This material was used as the starting material to fabricate a high ZT, nanostructured p-type material. The objective was to compare the ZT properties from multiple process methods and then determine which route produces the best microstructure and properties. Best P-type Nano-$Bi_xSb_{2-x}Te_3$

bulk alloy made by UTRC exhibited a ZT of 1.3 near 27°C.   Subsequent activities at UTRC were focused on delivering a material with a ZT~1.5. Spark plasma sintering was explored as an alternative consolidation technique to graphite hot pressing. The use of shorter milling times, cryo-milling, and low voltage SPS was also explored as various methods to reduce the final grain size.

Awards/Manuscripts/Presentations/IP

Papers published in peer-reviewed journals

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Presentations in meetings and not published in conference proceedings

1) F. Yang and C. Dames, "Thermal Conductivity Reduction in Bulk Nano-composites With Randomly Oriented Superlattice Grains," oral presentation at the 2010 Materials Research Society (MRS) Spring Meeting, San Francisco, CA.

2) F. Yang and C. Dames, "Thermal conductivity reduction in self-assembled lamellar materials with randomly oriented grains," oral presentation at the American Physical Society (APS) March Meeting 2010, Portland, OR.

3) Levin, L. M.; Hu, Y.-Y.; Cook, B. A.; Harringa, J. L.; Schmidt-Rohr, K.; Kanatzidis, M. G. , New insights into high-performance thermoelectric tellurides from 125Te NMR spectroscopy, American Physical Society, Inaugural Fall 2009 Meeting of the Prairie , Section of the APS, November 12-14, 2009, abstract #G2.007

4) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, Thin-film 2-di superlattices, Nano-dot Materials and Hybrid Nanostructures for Elevated Temperatures, Presentation at the 2010 Spring Materials Research Society Meeting, San Francisco, April 8, 2010.

5) R. Venkatasubramanian, Advanced Thermoelectrics for Portable Power, Energy Harvesting & Thermal Management (Invited Presentation), JHU/APL WALEX Advanced Portable Power Systems Workshop, Johns Hopkins University, Laurel, MD, June 24, 2010

6) R. Venkatasubramanian, G. Bulman, P. Barletta, J. Stuart & T. Colpitts, High Figure of Merit Thin-film Superlattice Thermoelectric Materials and Devices (Invited Presentation), 2010 CIMTEC, 5th Forum on New Materials, Montecatini, Italy, June 18, 2010.

7) R. Venkatasubramanian, Nanoscale Approaches to Thermoelectric Energy Conversion (Invited Presentation), South Eastern Section American Physical Society Meeting, Atlanta, GA, November 12, 2009.

Manuscripts under review and/or accepted for publication

1) Fang Fang, Robert L. Opila, Rama Venkatasubramanian and Thomas Colpitts, Valence Band Maxima Offset Measurements on Bi2Te3, Sb2Te3 Thin Films for Thermoelectric Superlattice Engineering, Submitted to Appl. Phys. Lett.,.

2) Tsung-ta E. Chan, James M. LeBeau, Rama Venkatasubramanian, Peter Thomas, Judy Stuart, and Carl C. Koch, "Carrier Concentration Modulation by Hot Pressing Pressure in N-type Nanostructured Bi(Se)Te Alloy," Accepted for publication in Applied Physics Letters.

3) Tsung-ta E. Chan, Rama Venkatasubramanian, James M. LeBeau, Ryan M. White, Peter Thomas, Judy Stuart, and Carl C. Koch, "High Efficiency Thermoelectric Devices Using Nanostructured Chalcogenide Alloy Materials," Under review for publication in Nature Nanotechnology.

Honors and Awards

1) R. Venkatasubramanian, R&D 100 Award, RTI International, June 2010

2) R. Venkatasubramanian, International Advisory Board, 2010 International Conference on Materials & Technologies, Italy, June 2010.

3) R. Venkatasubramanian, Focused Session Organizer – Thermoelectric Materials and Phenomena - March 2010 American Physical Society (APS) Meeting, Oregon.

4) R. Venkatasubramanian, Technical Program Committee Member – 2010 SPIE Meeting on Energy Harvesting and Storages: Materials, Devices, and Application.

5) Andrew May (Graduate Student, Caltech) received the Goldsmid Award for outstanding graduate work in thermoelectric, International Conference in Thermoelectrics, Shanghai China, May 2010.

6) Andrew May (Graduate Student, Caltech) received the Demetriades-Tsafka-Kokkalis Prize for outstanding graduate work in sustainable energy at Caltech, June 2010.

List of Patent Titles submitted/filed for patents

1) High Thermoelectric Performance in PbTe due to Large Nanoscale Ag2Te Precipitates and La Doping, Caltech.

2) N-type Nanocrystalline Bulk Bi2Te3-xSex Material with High Thermoelectric Figure of Merit (ZT), NCSU and RTI International

3) Improved Thermoelectric Alloys Based on $(AgSbTe_2)$-(GeTe) (TAGS)," Ames Lab and RTI International.

Technology Transfer and Insertion

This project directly resulted in a number of technology insertion opportunities for DoD and other application spaces. A few of these are highlighted, below.

1) Delta-doped n-type superlattice structures developed under NMP are being evaluated with DARPA/ACM support and partnership with United Technologies/Hamilton Sundstrand for thermal management of electronics in DoD aircraft systems for potential benefits in combat maneuver and maintenance cost reduction.

2) Fractional-scale demonstration of Waste Heat Energy Harvesting achieved ~80-Watts from a system deployment on an M1/A1 Abrams tank at General Dynamics Land Systems (GDLS) on a TE-system-related project with US Army. The advanced NMP materials will play a role in higher efficiency values in subsequent scale-up efforts. GDLS engineers report that a 5 to 25 kW waste-heat demo using TE on top of their typical "18-kW" alternator could significantly enable new operational capability. This may fit in areas such as higher efficiency of vehicles and generators in forward operational base, to reduce fuel usage.

3) On-board power for hypersonic vehicles via solid state energy harvesting. High-temperature thermoelectric energy conversion offers a unique approach to harvest energy from available waste heat in the operation of DoD hypersonic vehicles. The technology can reduce the dependence on batteries and reduce their weight contribution, leading to extended range. Recent demonstrations of NMP-generated TE technology, performed in collaboration with Wright-Patterson AFB and Lockheed-Martin Space Systems, have shown that power densities on the order of 3.5 W/cm^2 can be expected under typical thermal conditions encountered in hypersonic vehicles. Several potential locations offering adequate space and thermal profiles have been identified.

4) On-board power and thermal signature reduction in rotary aircraft platforms. Discussions were initiated with a major DoD supplier to investigate the use of NMP TE technology In rotary aircraft. The platform's engines produce on the order of 5MW of waste heat with primary exhaust nozzle temperatures on the order of 350°C to 450°C – thermal energy that not only could be converted into usable electrical power, but also increases the platform's thermal signature. High-efficiency TE energy harvesting modules offer an attractive, high-reliability solution.

Appendix

Summary of Relevant PRIOR Work

RTI: RTI has been involved in the area of nanoscale thermoelectric materials and realizing useful devices for more than a decade. RTI's key accomplishments are listed below:

1992 –Ideas on superlattice thermoelectrics to reduce thermal conductivity conceived at RTI

1993 –First funding for thermoelectrics work at RTI from Office of Naval Research and DOE

1994 –Thin-film materials and their superlattices demonstrated by MOCVD

1996 –First demonstration of thermal conductivity reduction with superlatices, compared to alloys

1997 –DARPA funds RTI to demonstrate a quantum jump in ZT and some early device technology

1999– DARPA funds Phase 2 to further validate SL materials and conclusively demonstrate enhanced ZT

2001– DARPA and Army Research Office fund development of SL power device technology

  – ZT ~2.4, large cooling power density, high-speed device results published in *Nature*

2002– RTI invests in commercializing TE technology with pilot-line tools

  – R&D 100 Award for Nanoscale Superlattice Thermoelectric Technology

  – RTI's thermoelectrics work nominated for Sustained Excellence Award by DARPA

  – Lockheed-Martin invests in RTI TE technology for IR coolers development

2003– RTI develops Bipolar Couples Assembled Module (BCAM) architecture for bulk materials

  – RTI begins an R&D co-development with a major microelectronics chip manufacturer

2004– DARPA funds RTI-led Direct Thermal Energy Conversion team for power device development

  – RTI demonstrates 7°C cooling in ▯P hot-spot SL cooler, hot-spot heat-flux over 1250 W/cm^2

  – RTI spin-off Nextreme Thermal to develop electronics cooling using SL and thin film TE

2005–RTI demonstrates >5W/cm^2 power density and near-20% efficiency in a complex 3-stage power conversion device employing SL low-temp stage, PbTe/TAGS mid-stage and SiGe top-stage

2006– RTI demonstrates a 14.6 W SL power module with ZT~1.42; X2 better than commercial bulk TE

  – Nextreme-RTI show 15°C cooling in ▯P hot-spot SL cooler, with heat-flux over 1250 W/cm^2

  – RTI demonstrates a 3-stage SL cooler with ▯T_{max} ~103K, 6K more than commercial bulk TE

2007–RTI demonstrates large-area, complex, 3-stage SL module can withstand 6G horizontal and vertical shear force and 25G vertical impulse force at Lockheed

–RTI demonstrates ~11% efficiency for PbTe/TAGS device at KAPL and using that as a calibration, estimates ~18% efficiency in an SL/PbTe-TAGS/SiGe 3-stage device

– RTI demonstrates scale up of all components for a 3-stage device and achieves 50Watt power level

– RTI demonstrates new N-type DDSL materials with better ZT as well as thick epi (~10 μm) SL

– RTI demonstrates a new device with p-SL/n-SL, overcoming p-n mismatch and with that device, UTRC model suggests that large ΔT_{max} (~120K) are occurring in p-SL elements consistent with large ZT

– NSWC and RTI show through XAS that there is very little static disorder in p-type SL materials

– Purdue and RTI show that femtosecond coherent phonon dephasing time is short, compared to that in alloys, and that phonon frequencies may be used to interpret presence of two components at nano scale

– UTRC and RTI demonstrate >10 W power level with BCAM devices in a scramjet rig at Mach 6.5

Cal Tech: Dr. Snyder at Caltech has pioneered the formation and control of bulk nanostructured thermoelectric materials with demonstrated control of the nanometer layer spacings in bulk Sb_2Te_3/PbTe composites with epitaxy-like interfaces. Using *in situ* measurements of thermoelectric properties while the nanometer-scale microstructure is forming, Caltech has unequivocally demonstrated a continuous reduction in lattice thermal conductivity as the layer spacing decreases. Cal Tech's work has also lead to the discovery of the best high temperature p-type material $Yb_{14}MnSb_{11}$. Prof. van de Walle group has recently developed automated formal statistical algorithms, based on cross-validation and variance minimization, the enable the construction of optimal cluster expansions using ab initio electronic structure calculations. Prof. Goddard group has successfully described of the electric band structures by combining the QM and the tight-binding study including spin-orbit coupling to achieve for the first time the correct band gap in Sb_2Te_3. (0.26eV vs. 0.28eV).

Purdue University: The prior work at Purdue University relevant to the proposed work including (1) developing a photoacoustic method for measuring thermal conductivity. This method has been used to measure nanostructured bulk materials, thin films (~ 0.1 μm and above), and interface resistances. Fs thermoreflectance technique has been used to measure thermal conductivity of TE materials from RTI. Ultrafast coherent phonon excitation and measurement for understanding ultrafast energy transport process in thermoelectric materials.

UTRC: UTRC in collaboration with RTI, on the DTEC program, designed, fabricated and tested TE device configurations in UTRC's scramjet combustor rig. These tests simulated realistic engine conditions at a representative condition above Mach 6 and 12 Watts was demonstrated. On a DARPA/TTO program, UTRC, in collaboration with Hamilton Sundstrand, BSST, and Battelle Memorial Institute, led a 6-month seed program entitled "Thermoelectric Cooling, Heating and Portable Power for Soldiers". The final configuration of the thermoelectric subsystem will be capable of providing either cooling or heating to enhance the soldier's comfort level and thus improve operational capabilities over a wide range of ambient conditions (40°F to 120°F).

Ames: Dr. Cook has developed novel processing techniques for improved thermoelectric materials, including TAGS, PbTe, Bi_2Te_3, and Skutterudites, and has successfully integrated these approaches in prior support for RTI-led programs. He has over 15 years of experience in synthesis and characterization of TE materials, having received an Outstanding Achievement Award from NASA for his work on development of improved TE materials for remote space missions. Dr. Cook has also led the effort to establish the structure-property correlations between nanoscale inclusions in complex quaternary chalcogenides of the form $AgPb_xSbTe_{2+x}$ and the materials high thermoelectric figure-of-merit (ZT) through the use of TEM, EPMA, high temperature XRD, and most recently, NMR.

UCR: Prof. Dames has extensive experience with semiclassical modeling of phonon thermal transport in nanostructures. Using a frequency-dependent form of kinetic theory with no free parameters [6], they explained the experimentally-reported 1000-fold reduction in the thermal conductivity of silicon nanowires compared to bulk silicon. This model also quantifies for the first time the surprisingly large contributions of phonons with long mean free paths to the thermal conductivity. This result shows that there is much greater potential for thermal conductivity reduction by interface/boundary scattering in nanostructured materials than is generally appreciated. Prof. Dames has also studied the altered phonon dispersions due to quantum confinement effects in nanostructures of characteristic length < 3 nm, both theoretically and experimentally [45].

UD: Prof. Opila's group at UD has performed a great deal of work determining the band alignment for a variety of systems. For example, in next generation MOSFET transistors the alignment of the valence and conduction bands of the high-k dielectric, the Si substrate, and the metal gate electrode all contribute to the leakage of the transistor. We have used photoemission to confirm the band-line up of a variety of candidate metal gates with candidate high-k dielectrics including nitrided hafnium silicate deposited on p-type and n-type Si. We are currently studying charge transfer between promising molecules and semiconductor substrates for moletronics. Charge transfer depends upon the relative positions of the HOMO and LUMO and the valence and conduction bands of the substrate, which depends upon the doping of the substrate and the structure of the chemisorbed molecule. Similarly charge collection in photovoltaics depends upon band alignment between electrodes and p-type and n-type components. We have developed state of the art software, which permits photoelectron spectroscopy to non-destructively determine the composition as a function of depth. IPES that permit direct measurement of the conduction bands exists at UD.

NCSU: NCSU has many years experience in the synthesis of materials using the non-equilibrium processing method of mechanical attrition (ball milling of powders). For over 20 years this group has become a leader in the field of amorphous and nanocrystalline materials prepared by mechanical milling and mechanical alloying. The research has been supported by BES-DOE, ONR, and continuously, by NSF-DMR. The Co-PI, C. C. Koch is responsible for the first amorphous metallic system made by mechanical alloying and in recent years has produced nanocrystalline materials with superior structures and properties (Applied Physics Letters, 87 (2005) 091904-1.

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